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COMPLEXOMETRIC

TITRATIONS

COMPLEXOMETRIC TITRATIONS

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To

JANNIK BJERRUM

Professor Jannik Bjerrum, of the Technical University of Denmark at Copenhagen, discovered the step-wise formation of complexes. We are indebted to him for many reliable measurements of the stabilities of metal complexes, and at the present time he is working on a compilation of all the published formation constants. This little book shows how useful a knowledge of such data can be to the analytical chemist

Contents

PREFACES *page* xi

LIST OF SYMBOLS xv

1. POLYAMINES AND COMPLEXONES

1.1. Introduction 1
1.2. Polyamines 2
1.3. Complexones 6

2. BASIC THEORY OF COMPLEXOMETRIC TITRATIONS

2.1. Complex Formation 10
2.2. Survey of Different Types of Complexometric Titrations 11
2.3. Titration Curves of Complexometry 15

3. INDICATORS USED IN COMPLEXOMETRY

3.1. Metal Indicators 29
3.2. pH Indicators 46
3.3. Redox Indicators 47
3.4. Photometric End-points 49

4. TITRATION OF MIXTURES

4.1. Ions which form Complexes of Widely Differing Stability 50
4.2. Use of Masking Reagents 51
4.3. Precipitation and Solvent Extraction 53
4.4. Use of Ion-Exchange Resins 54

5. SOLUTIONS USED IN COMPLEXOMETRIC TITRATIONS

5.1. Standard Solutions 55
5.2. Indicators 57
5.3. Buffers 58
5.4. Masking and De-Masking Agents; Oxidising and Reducing Agents 59

6. DETAILS OF PROCEDURES

6.1. Alkalimetric Titrations of Metals with EDTA 60
6.2. Alkalimetric Titrations of Metals with NITA 61

6.3. Iodometric Finish to Procedure 6.2 *page* 61
6.4. Direct Titration of Magnesium with Erio T 62
6.5. Substitution Titration for Calcium using Erio T as Indicator 63
6.6. Determination of the Total Concentration of Calcium and Magnesium using Erio T; Hardness of Water 64
6.7. Substitution Titration for Strontium and Barium using Erio T 66
6.8. Direct Titration of Calcium using Murexide 69
6.9. Direct Titration of Calcium using Metalphthalein 71
6.10. Direct Titration of Barium (or Strontium) using Metalphthalein 72
6.11. Direct Titration of Rare-Earths using Erio T 73
6.12. Back-titration of Zirconium with Ferric Iron using Salicylic Acid 74
6.13. Direct Titration of Thorium using Pyrocatechol Violet 75
6.14. Substitution Titration of Manganese using Erio T 76
6.15. Direct Titration of Ferric Iron using Tiron, Salicylic Acid, or Thiosalicylic Acid 77
6.16. Direct Titration of Ferric Iron using Variamine Blue 78
6.17. Direct Titration of Cobalt with Murexide 78
6.18. Back-titration of Cobalt using Erio T 79
6.19. Direct Determination of Nickel with Murexide 79
6.20. Back-titration of Nickel using Erio T 81
6.21. Direct Titration of Copper using Murexide 82
6.22. Titration of Zinc and Cadmium using Erio T 83
6.23. Titration of Zinc using Dimethylnaphthidine 87
6.24. Substitution Titration for Mercury using Erio T 87
6.25. Back-titration of Aluminium using Erio T 88
6.26. Back-titration of Aluminium with Ferric Iron using Salicylic Acid as Indicator 89
6.27. Direct Titration of Indium using Erio T 91
6.28. Substitution Titration for Thallium using Erio T 91
6.29. Titration of Lead using Erio T 92
6.30. Direct Titration of Bismuth using Pyrocatechol Violet 93
6.31. Indirect Titration of Sodium 94
6.32. Indirect Titration of Phosphate 95
6.33. Indirect Determination of Sulphate 96

6.34. Indirect Determination of Cyanide *page* 97
6.35. Indirect Determination of Silver, Halides, and Thiocyanate 98
6.36. Indirect Determination of Palladium 100

7. CONCLUDING REMARKS 101

BIBLIOGRAPHY 107

INDEX 127

Translator's Preface

My first task is to express my deep gratitude to Prof. Schwarzenbach for granting me the privilege of writing an English translation of his monograph on 'Complexometric Titrations' and thus playing some small part in bringing this fine work to the attention of a wider public.

If the rapidly expanding list of original papers devoted to complexometric titrations were not itself a sufficient indication, the fact that copies of the first German edition of Schwarzenbach's book were sold out six months after it first appeared in 1955 provides a clear proof of the widespread and growing interest in this important new field of analytical chemistry. In the past eighteen months new metal indicators and new masking agents have been developed, and the complexones* have secured a firm footing in polarographic, amperometric, and photometric procedures. The latest development is the electrolytic preparation of EDTA from its mercury complex which permits the determination of a variety of metals by coulometric procedures.†

The task of revising and augmenting the original MSS for the preparation of a second German edition has run parallel to that of preparing this English translation and it has proved possible to incorporate all the corrections and new material in the present work. In doing so I have taken the opportunity of regrouping the text in seven chapters and I have renumbered the equations throughout in such a way as to facilitate cross-referencing. Some of the absorption spectra in the original book have had to be revised in the light of new measurements, and new diagrams have been provided. Some new procedures have been added and the bibliography has been extended from 181 to 305 entries, making it complete up to August 1956. The index has been revised and greatly enlarged.

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* The term *complexone* (plural *complexones*) is used throughout this book in accordance with established scientific usage to denote a complexing agent of the type of a polyaminocarboxylic acid, or a related salt. The word "Complexone" is also registered as a Trade-mark and reserved for certain commercial products marketed by the Uetikon Chemical Company, Switzerland. In America various complexones are marketed under the trade name of "Versenes" and similar trade products appear in England under such names as "Nervanaid", "Sequestric Acid" etc.

† C. N. Reilley *et al.*, *Anal. Chem.*, 1956, **28**, 443, 520.

I have great pleasure in acknowledging my debt to Dr. L. M. Venanzi for his critical reading of all the page proofs.

H. IRVING

The Inorganic Chemistry Laboratory,
Oxford
October, 1956

Preface to the First German Edition

Quantitative studies were started some ten years ago on the complexes which metals form with nitrilotriacetic acid and ethylenediaminetetra-acetic acid. The high stability of these complexes and their simple composition indicated the possibility of using such aminopolycarboxylic acids ('complexones') as reagents in volumetric analysis, and a suggestion to this effect was first made in a lecture entitled 'Acids, Bases, and Complexing Agents' which I gave to the Swiss Chemical Society in the Spring of 1945.* On that occasion a comparison was drawn between metal cations—regarded as Lewis acids—and the hydrogen ion, and between chelating agents—which can be regarded as Brønsted bases—and the hydroxyl ion. Demonstrations were given of the abrupt changes in pH which occur at the end-point of a titration when salts of heavy metals are treated with an alkaline solution of the alkali-metal salts, Na_3X or Na_4Y, of the aminocarboxylic acids mentioned above.

Uramildiacetic acid[220] was one of the many different derivatives of iminodiacetic acid which we synthesised about that time and then investigated quantitatively. It was obtained from aminobarbituric acid; but the reaction mixture was frequently coloured red by small amounts of murexide formed by atmospheric oxidation. The change of colour produced by calcium ions was observed, quite by chance, when washing-up the reaction vessels in hard tap-water, and an investigation of this phenomenon enabled me to recognise the analogy to acid-base indicators. This was how the idea of metal-indicators originated[215]. Murexide was naturally introduced at once for the titration of calcium[211], and a search was instituted for further metal-indicators. We gave particular attention to the range of commercial mordant and chrome dyestuffs, and guided by information from C. Brenner, Walter Biedermann was led to examine the group of Eriochrome dyestuffs. Measurements of the relevant equilibrium constants proved Eriochrome Black T to be the most suitable dyestuff of this group for our purpose, and in this way the most important metal-indicator was discovered[210].

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* *Schweiz. Chemiker-Zeitung*, 1945.

The direct volumetric determination of the hardness of water, using Erio T as indicator, was first reported[12] in January, 1948. But this paper provoked no immediate repercussions, and the first of the many publications dealing with this topic from other laboratories, and particularly from American laboratories, did not appear until two years later[46, 48, 85, 140, 141, 250]. Thereafter the subject developed with a rush, and there are today already some 300 papers dealing with the field of 'complexometric titrations'. Titrations of the alkaline-earth metals are still of special importance. Indeed, the applications of complexometry to the determination of heavy metals appeared somewhat slowly, and at first it was something of a deterrent that the various complexones and metal indicators were very unselective in their reactions. Quite early on we pointed out the possibilities opened up by masking interfering ions with, *e.g.* cyanide[12]. But we are indebted to other workers, especially H Flaschka, R. Přibil, and J. Kinnunen for important improvements in procedures for the simultaneous determination of several metals, and for various indirect methods. There are already a number of comprehensive accounts of the practice of complexometry[26, 52, 66, 67, 68, 102, 129, 135, 143, 152, 166] and a booklet by Přibil[171], but the basic theory of these new types of titration procedures has never yet been presented although this year (1955) marks the tenth anniversary of their discovery. Clearly it is high time to repair this omission, to survey what has been achieved, and to consider future developments. This little book should show how a grasp of the theory underlying complexometric titrations can lead to further advances in laboratory practice.

The author has been fortunate in obtaining a good deal of help in developing the new field of complexometry. Above all he would like to express his thanks to his collaborators and pupils, especially to H. Ackermann, G. Anderegg, W. Biedermann, H. Gysling, and A. Willi. He extends his warmest thanks to Dr. Přibil, Dr. Flaschka, and J. Kinnunen who have corresponded with him time and time again about their latest developments. Finally he is happy to express his heartfelt gratitude to the Federal Foundation for the Advancement of Swiss Political Economy through Scientific Research, to the Uetikon Chemical Company, Uetikon (Switzerland), and to the firm of J. R. Geigy & Co, of Bâle, who provided generous financial support for these investigations.

Zurich, Winter, 1954–55

GEROLD SCHWARZENBACH

LIST OF SYMBOLS USED IN TEXT

(with references to the page or equation where they are first introduced)

ABBREVIATIONS

$M^{+\nu}$	A metal cation carrying a charge of $+\nu$. (p. 9)
$A^{-\lambda}$	A monodentate complexing agent, *e.g.* NH_3, OH^-, acetate ion, etc. (p. 15)
$Z^{-\mu}$	The general symbol for any chelating agent, *e.g.* a molecule of a polyamine, or the anions of NITA or EDTA (see below), or the coloured anion of a metal-indicator. (pp. 7, 10)

The following special symbols are also used:

tren	Tri-(2-aminoethyl)amine. (p. 2)
penten	*NNN′N′*-tetra-(2-aminoethyl)ethylenediamine. (p. 2)
NITA	Nitrilotriacetic acid in any form. (p. 7)
EDTA	Ethylenediaminetetra-acetic acid in any form. (p. 7)
X^{-3}	The anion of NITA. (pp. 7, 9)
Y^{-4}	The anion of EDTA. (pp. 7, 9)
$D^{-\mu}$	The anion of a dyestuff used as a metal-indicator. (p. 29)

STOICHEIOMETRY

n	The number of ligands in the complex $MA_n^{\nu-n\lambda}$. (p. 3, Eq. 1.5)
N	The maximum possible value of n for a particular metal. (p. 3)
j	The number of ionisable hydrogen atoms in the species $H_jZ^{j-\mu}$. (p. 8, Eq. 1.9)
J	The maximum possible value of j in strongly acid solution. (p. 11, Eq. 2.8)

CONCENTRATIONS

[ ]	This symbol denotes the concentration, in moles per litre, of the species enclosed in the square brackets. Thus [M] denotes the concentration of free, completely solvated metal ions. The charge on the particle is omitted on grounds of generality.

pM	$= -\log_{10}[M]$. (pp. 4, 12)
$[\ ]_t$	The total concentration of a species as determined by analysis. Thus $[M]_t$ represents the total concentration of metal in solution and includes the concentration of free ions and of all complexes containing M. (p. 16, Eq. 2.16) Similarly $[Y]_t$ represents the total concentration of EDTA and includes that of the free ions Y^{-4}, the hydrogen complexes HY^{-3}, H_2Y^{-2}, H_3Y^- and H_4Y, and all the possible metal complexes which may be present. (p. 16, Eq. 2.18)
$[\ ]'$	This symbol distinguishes the total concentration of a particular element or group. For example:
$[M]'$	$= \sum_{n=0}^{N} [MA_n]$, and denotes the total concentration of metal present as the simple ion, M, or combined with the monodentate partner, A. It does *not* include the concentration of any metal combined with a polydentate chelating agent such as EDTA or NITA. (p. 16, Eq. 2.17)
$[Z]'$	$= \sum_{j=0}^{J} [H_jZ]$, and denotes the total concentration of a chelating agent such as EDTA which is *not* bound to a metal. (pp. 6, 11 Eq. 2.8)
$[H]'$	$= \sum^{J} j[H_jZ]$, and denotes the total concentration of acidic hydrogen *not* present as free hydrogen ions. (p. 25, Eq. 2.29)

EQUILIBRIUM CONSTANTS

K, κ	Concentration (stoicheiometric) equilibrium constants governing the equations of mass-action. They are valid only for a particular, specified ionic strength, μ, and for a particular temperature. All the data in this book refer to $\mu = 0{\cdot}1$ and to 20°C. (p. 3, Eq. 1.6)
K	Denotes the equilibrium constants for individual stages in a stepwise reaction. More specifically:
K_{H_jZ}	$= [H_jZ]/[H][H_{j-1}Z]$ is the individual or stepwise formation (or stability) constant for the species H_jZ. It is, of course, the equilibrium constant for the process: $H^+ + H_{j-1}Z^{j-1-\mu} \rightarrow H_jZ^{j-\mu}$. (p. 8)

K_{MA} $= [MA_n]/[A][MA_{n-1}]$ is the individual formation (or stability) constant for the species MA_n. It is the equilibrium constant for the process:

and will often be abbreviated to K_n. (p. 3, Eq. 1.5)

κ Denotes the gross, or over-all constant for a series of step reactions. For example:

κ_{HjZ} $= [H_j$

$$= \prod_{j=1}^{j}$$

It is the equilibrium constant for the over-all reaction:

$$Z^{-\mu} + jH^+ \rightarrow H_jZ^{j-\mu}. \text{ (p. 8, Eq. 1.9)}$$

κ_{MA_n} $= [MA_n]/[M][A]^n = K_{MA} \cdot K_{MA_2} \cdot K_{MA_3} \ . \ . \ . \ K_{MA_n}$

$$= \prod_{n=1}^{n}$$

This is the equilibrium constant for the over-all reaction:

and will often be abbreviated to K_n. (p. 3, Eq. 1.6)

K_{MZ} $= [MZ]/[M][Z]$ is the formation constant of the chelate complex, MZ. It is unnecessary, as a rule, to distinguish between the step-constants and the over-all constants here, since no higher complexes such as MZ_2, MZ_3, etc., need be taken into consideration. (p. 7, Eq. 1.8)

Three different *apparent formation constants* of the chelated complex, MZ, valid for a particular concentration of ligand and hydrogen ion (which are usually specified by subscripts) are defined as follows:

$K_{M'Z}$ $= [MZ$

$K_{MZ'}$ $= [MZ]/[M][Z]'$. (pp. 6, 11, Eq. 2.7)

$K_{M'Z'}$ $= [MZ]/[M]'[Z]'$. (pp. 13, 16, 24, Eq. 2.22)

DIMENSIONLESS COEFFICIENTS

a This denotes the number of moles of titrant per mole of the constituent being titrated which have been added at

	any stage in a titration. *E.g.* the number of moles of EDTA per mole of metal, or the number of moles of NaOH per mole of acid. At the equivalent point (end-point), *a* is therefore a whole number, 1, 2, ... (p. 15)
α_{H}	The value of the quotient [Z]′/[Z] at any given hydrogen-ion concentration. Since $\alpha_{\mathrm{H}} = \Sigma[\mathrm{H}_j\mathrm{Z}]/[\mathrm{Z}] = \Sigma\kappa_{\mathrm{H}}$ its numerical value is a function only of the pH and of the stability constants of the proton complexes, $\mathrm{H}_j\mathrm{Z}$, (cf. Fig. 2) and not directly dependent upon the actual concentration of complexing agent. (p. 11, Eqs. 2.8, 2.9)
β_{A}	The value of the quotient [M]′/[M] when the concentration of free ligand is [A]. Since $\beta_{\mathrm{A}} = \Sigma\kappa_{\mathrm{MA}_n}[\mathrm{A}]^n$, it is a function only of [A] and of the stability constants of the relevant metal complexes. (p. 16, Eqs. 2.17, 2.21)
γ_{H}	$= [\mathrm{H}]'/[\mathrm{Z}] = \sum j[\mathrm{H}_j\mathrm{Z}]/[\mathrm{Z}] = \Sigma j\kappa_{\mathrm{H}_j\mathrm{Z}}[\mathrm{H}]^j$ is the distribution coefficient of acidic protons with respect to the complexing agent, Z, at the particular hydrogen-ion concentration, [H]. (p. 26, Eq. 2.31)

CHAPTER ONE

Polyamines and Complexones

1.1. Introduction

A reaction can only serve as a basis of a titration procedure if the following conditions are satisfied:

(i) The reaction must be a fast one;
(ii) it must proceed stoichieometrically;
(iii) the change in free-energy must be sufficiently large.

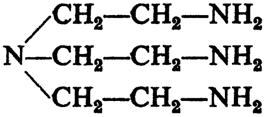
Should these conditions be fulfilled, it is generally possible to ascertain the end-point of the reaction, either by using the colour change of an indicator, or potentiometrically with an indicator electrode, or by measurements of conductivity or of the diffusion current at a dropping mercury electrode.

However, when dealing with the formation of metal complexes, the three requirements stated above are not, in general, completely met. On the one hand, with stable 'penetration complexes' such as those formed by Cr(III) or Co(III), we have to deal with relatively slow reactions. On the other hand, although the countless 'ordinary' complexes are formed practically instantaneously from their components, they are but loosely associated and weak complexes, so that the third condition is not fulfilled. Hg^{+2}, Ag^{+}, and Ni^{+2} form exceptions to this generalisation and their ability to form complexes, especially with cyanide ion, has long since formed the basis of a few volumetric procedures[128].

Generally speaking, the formation of ordinary complexes fails to satisfy condition (ii) as well as (iii). The replacement of the water molecules in the hydration sheath of a metal ion by other ligands such as NH_3 or CN^- invariably takes place in a series of discrete steps[18]. Consequently the reaction acquires a definite resemblance to the neutralisation of a polybasic acid which likewise proceeds in stages. Therefore as successive molecules of the complex-forming partner, A, become attached to the central ion, M, there results a whole series of different complex species MA, MA_2, . . . MA_N and, as a rule, several are present simultaneously in appreciable concentrations since the successive stages overlap. Complex formation is not then complete until after a certain excess of the complexing agent has been added. On this account the end-point is characterised neither by a rapid decrease in the concentration of metal ions, nor by a rapid rise in the concentration of free ligand. It is as gradual and drawn-out as the end of the neutralisation of a very weak polybasic acid, *e.g.* a polyphenol[195, 197].

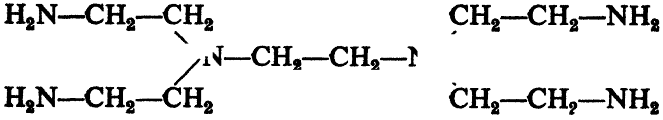
1.2. Polyamines

A more favourable state of affairs can be achieved if all the ligands needed by any one metal atom are linked together. In place of several discrete molecules of ammonia, suppose we bring up to the metal cation an organic polyamine whose basic nitrogen atoms are attached to a carbon skeleton in such a way that 5- or 6-membered chelate rings can be formed when complex formation takes place[195]. Take for example the tetramine (I) and the hexamine (II), for which the abbreviations 'tren' and 'penten' will be used[185, 221].



(I: 'tren')

pK's = 10·29; 9·69; 8·56



(II: 'penten')

pK's = 10·20; 9·70; 9·14; 8·56

There are two consequences of using such a complexing agent[142]. In the first place, the stoichieometry of complex formation is simplified and simultaneously the step-wise formation is eliminated[197], for the cation no longer needs four or six separate molecules of ammonia

$$^{2} \; . \; . \; . \rightarrow \mathrm{Ni(NH_3)_6}^{+2} \quad . \quad (1.1)$$

but only a single molecule of polyamine

$$\mathrm{Ni}^{+2} + \text{penten} \rightarrow \mathrm{Ni(penten)}^{+2} \quad . \; . \; . \quad (1.2)$$

In the second place, there is an advantage gained by the 'chelate effect'. This is a term used to describe[198] the enhanced stability of a chelated complex when compared with that of the corresponding complex with monodentate ligands[110]. The logarithm of the ratio of the equilibrium constants of the two relevant reactions provides a quantitative measure of the magnitude of the chelate effect. Thus for reactions (1.1) and (1.2) we have[13, 221]

$$K_1 = \frac{[\mathrm{Ni(NH_3)_6}]}{[\mathrm{Ni}][\mathrm{NH_3}]^6} = 3{\cdot}1 \times 10^8, \text{ and } K_2 = \frac{[\mathrm{Ni(penten)}]}{[\mathrm{Ni}][\mathrm{penten}]} = 2 \times 10^{19} \quad . \; . \; . \; . \; . \; . \; (1.3)$$

so that for this particular case the chelate effect is given by

$$\text{Chel.} = \log K_2 - \log K_1 = 10{\cdot}8 \quad . \; . \quad (1.4)$$

As shown by the numerical data in this example, the chelate effect attains astonishingly high values. This is true not only in the case of nickel but quite generally, as shown in Table 1. Columns 2 to 7 of this Table give the formation constants, K_n of the individual ammonia-complexes, $M(NH_3)_n$ for a number of cations[13]. These are defined by

$$K_n = [M(NH_3)_n]/[M(NH_3)_{n-1}][NH_3] \quad . \; . \; . \; (1.5)$$

where n can take all values from 1 to the maximum coordination number N. These individual constants show the pattern of step-wise complex formation with ammonia. The product of the individual constants is identical with the so-called gross or over-all formation constant of the complex under consideration. Thus

$$\kappa_n = [M(NH_3)_n]/[M][NH_3]^n = \qquad K_n = \prod K_n \quad (1.6)$$

and the values appropriate for $n = 4$, and $n = 6$ are shown in columns 8 and 9 of Table 1. The values of the constants κ_4 and κ_6

TABLE 1

Formation constants for ammine-complexes at 20°C in a medium of ionic strength 0·1. (References 13, 185, 221)

1	2	3	4	5	6	7	8	9	10	11
Cation	log K_1	log K_2	log K_3	log K_4	log K_5	log K_6	log κ_4	log κ_6	log $K_{M(tren)}$	log $K_{M(penten)}$
Zn	2·27	2·34	2·40	2·05	—	—	9·06	—	14·65	16·24
Cu	4·13	3·48	2·87	2·11	—	—	12·59	—	18·8	22·4
Ni	2·75	2·20	1·69	1·15	0·71	− 0·01	7·8	8·5	14·4	19·3
Cd	2·60	2·05	1·39	0·88	−0·3	− 1·7	6·92	4·92	12·3	16·8
Ag	3·2	3·83	—	—	—	—	—	—	7·8	—

should be compared with those of the formation constants $K_{M(tren)}$ and $K_{M(penten)}$ of metal complexes with the organic tetramine[185] and hexamine[221] when the magnitude of the chelate effect is to be computed.

Fig. 1 gives an idea how the chelate effect can influence a titration[197]. Nickel has again been chosen as the example and its titration first with ammonia, and then with the hexamine 'penten' (II) is represented. The number of atoms of amino nitrogen added per gram ion of Ni^{+2} is shown along the abscissa. The ordinates give the value of $pNi = -\log_{10}[Ni]$; this corresponds to the pH in an acid-alkali titration.

The addition of a basic amine to an unbuffered solution of the metal salt changes not only the concentration of the nickel but also the pH which, of course, causes a transient precipitation of nickel hydroxide. Such precipitation can be avoided if the titration is carried out in the presence of a considerable excess of ammonium chloride which ensures that the pH only rises slowly. These considerations led to the following conditions for the titrations shown in Fig. 1.

Curve A represents the titration of the nickel solution with NH_3 in the presence of 0.1M–NH_4Cl. At the point of equivalence ($a = 6$ moles of NH_3 per Ni) the concentration of free nickel ion has only fallen to one-fifth of its original value, and this point is not characterised by an abrupt jump in pNi. Complex formation is not effectively completed until a vast excess of ammonia has been added.

Quite a different state of affairs is depicted in Curve B which represents the titration of nickel, still in the presence of 0.1M–NH_4Cl, with the hexamine 'penten'. Quite a respectable jump in pNi is found here. However, it does not coincide exactly with the stoichieometric end-point but appears too late; moreover, the pH begins to rise steeply as soon as all the nickel has been bound up as complex, whereat the stability of the penten-complex rises too.

When carrying out a titration with a complexing agent it is much better to maintain the pH constant, and to choose a high value for it. This is demonstrated by Curve C which depicts the titration of nickel with 'penten' in the presence of both ammonium chloride (0.1M) and ammonia (0.1M), *i.e.* in a buffer of pH about 9·3. Adding the ammonia changes the nickel into a mixture of its ammine complexes and thereby reduces the concentration of free nickel ions so that the titration begins not at pNi = 3, but at pNi = 6·9. During the titration the ammonia-complexes are transformed into the penten-complex and finally there is a pronounced increase in pNi, coinciding exactly in this instance with the stoichieometric end-point. The jump in pNi embraces fully six logarithmic units and is therefore somewhat greater even than the jump in pH obtained when HCl is titrated with NaOH.

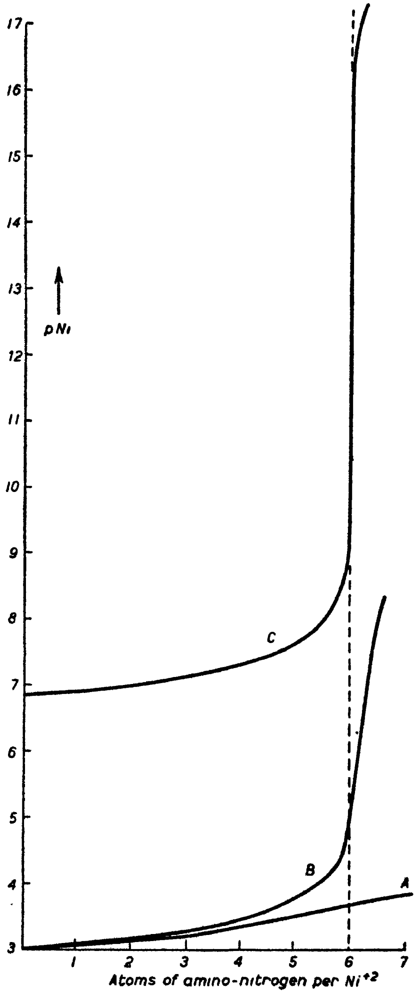


FIG. 1. The titration of Ni^{+2} with amines

Curve A. Titration of Ni^{+2} with ammonia in the presence of 0.1M–NH_4Cl.
Curve B. Titration of Ni^{+2} with 'penten' in the presence of 0.1M–NH_4Cl.
Curve C. Titration of Ni^{+2} with 'penten' in the presence of 0.1M–NH_4Cl and 0.1M–NH_4OH. In each case $[Ni]_t = 10^{-3}$. The curves have been calculated from the constants given in Table 1, using equations analogous to those developed in section 2.3.

The examples shown in Fig. 1 prove that, in point of fact, titrations can be carried out using organic polyamines as titrant. These procedures would, however, remain restricted to those metal cations which show a pronounced tendency to coordinate through basic nitrogen atoms, *i.e.* to Cu, Ni, Co, Zn, Cd, and Hg in particular. A further disadvantage attaching to polyamines is that their metal complexes are very sensitive to acids since the chelating agent is able to take up several protons. Thus the hexamine 'penten' occurs as the tetra-ammonium ion even at pH = 7 so that the metal cation has to displace four protons when it forms a complex; thus

$$\mathrm{Ni}^{+2} + \mathrm{H_4penten}^{+4} \leftarrow \mathrm{Ni(penten)}^{+2} + 4\mathrm{H}^{+} \quad . \quad . \quad (1.7)$$

This reaction (1.7) therefore takes place at pH = 7 in preference to that represented by equation (1.2), and instead of the equilibrium constant K_2 of (1.3) we obtain the very much smaller *apparent stability constant* of the complex which, at pH = 7, assumes the following value:

$$(K_{\mathrm{Ni(penten)'}})_{\mathrm{pH}=7} = \frac{[\mathrm{Ni(penten)}]}{[\mathrm{Ni}][\mathrm{penten}]'} = 4{\cdot}9 \times 10^{9}$$

Here the symbol [penten]′ signifies the total concentration of complexing agent which is not coordinated to the nickel; thus

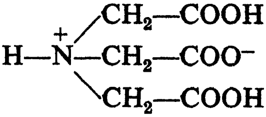
$$[\mathrm{penten}]' = \sum_{j=0}^{4} [\mathrm{H}_j\mathrm{penten}]$$

Despite these circumstances the polyamines remain interesting reagents for complexometric procedures and permit a number of selective titrations to be carried out. Unfortunately they are, up to the present time, difficult to obtain completely pure, so that their potentialities as titrating agents have only been studied to a limited extent.

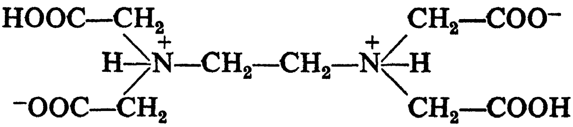
1.3. Complexones[196, 200–203, 205, 207–214, 216–220, 222, 226]

Nowadays, the complexing agents used exclusively in complexometry are aminopolycarboxylic acids among which ethylenediaminetetra-acetic acid (EDTA) has pride of place. Only for titrations of Type IV (section 2.2.4.) is nitrilotriacetic acid (NITA) somewhat more suitable. Some data on the analytical applications of certain other complexones which we have investigated will be found in Chapter 7.

The anions of these acids will be designated X^{-3} and Y^{-4} respectively. In order not to overload the symbols, charges on these species will be omitted in mass-action expressions. The symbol $Z^{-\mu}$ will be used to denote any sort of complexing agent: it can therefore represent both X^{-3} and Y^{-4}, as well as any other aminopolycarboxylic acid or a polyamine.



Nitrilotriacetic acid (III)
NITA or H_3X
pK's = 1·9; 2·49; 9·73[203]



Ethylenediaminetetra-acetic acid (IV)
EDTA or H_4Y
pK's = 2·0; 2·67; 6·16; 10·26[201]

The anions of NITA and EDTA have respectively four or six atoms available for coordination to a metal cation in such a way that five-membered chelate rings are produced; the ion X^{-3} has a basic nitrogen atom and three carboxylic oxygens; the ion Y^{-4} has two basic nitrogens and four carboxylate groups. Comparison with 'tren' (I) and 'penten' (II) shows that the terminal amino-groups are replaced by carboxyl groups in these complexones. The ability of the grouping $-\ COO^-$ to coordinate to a metal ion can be judged from the behaviour of the acetate ion[14]. Acetato-complexes are admittedly not very stable, but they are formed by practically all the polyvalent cations. When, in addition, the general tendency towards complex formation is reinforced by the chelate effect (section 1.2), as is the case with the anions X^{-3} and Y^{-4} ,there should result powerful complexing agents of low selectivity, *i.e.* substances which should react with practically every metal cation. In actual fact the aminopolycarboxylic acids form complexes even with the rare-earth metals, and with the alkaline-earth metals, and to a slight extent with Li^+ and Na^+ too. Table 2 summarises the logarithms of the stability constants of the complexes $MX^{\nu-3}$ and $MY^{\nu-4}$ which are defined by the following equation:

$$K_{MZ} = [MZ]/[M][Z] \quad . \quad . \quad . \quad . \quad . \quad (1.8)$$

Below the structural formulae for NITA (III) and EDTA (IV) are given their pK values. These are to be interpreted as the logarithms of the stability constants of the proton complexes HX^{-2}, H_2X^-, H_3X

TABLE 2

(References 1, 200, 201, 203, 212–214, 216–218, 222, 244)

The stability constants of complexes formed by EDTA and by NITA, valid for a medium of ionic strength μ = 0·1 at 20°C

Cation	log K_{MY}	log K_{MX}	Cation	log K_{MY}	log K_{MX}
H^+ j = 1	10·26	9·73	Hg^{+2}	21·80	
j = 2	6·16	2·49	Pb^{+2}	18·04	11·39
j = 3	2·67	1·9	V^{+2}	12·7	
j = 4	2·0		VO^{+2}	18·77	
			Eu^{+2}	7·7	
Mg^{+2}	8·69	5·41	Al^{+3}	16·13	
Ca^{+2}	10·70	6·41	Fe^{+3}	25·1	15·87
Sr^{+2}	8·63	4·98	Y^{+3}	18·09	11·41
Ba^{+2}	7·76	4·82	La^{+3}	15·50	10·48
Mn^{+2}	13·79	7·44	Lu^{+3}	19·83	12·2
Fe^{+2}	14·33	8·84	Sc^{+3}	23·1	
Co^{+2}	16·31	10·38	V^{+3}	25·9	
Ni^{+2}	18·62	11·53	Ga^{+3}	20·3	
Cu^{+2}	18·80	12·96	In^{+3}	24·9	
Zn^{+2}	16·50	10·67	Th^{+4}	23·2	
Cd^{+2}	16·46	9·83	Ag^+	7·3	5·4

The stability constants of the tervalent rare-earth complexes lie between those for La^{+3} and Lu^{+3}.

and HY^{-3}, H_2Y^{-2}, H_3Y^-, H_4Y respectively, and they have therefore been included in Table 2. They are defined by the following equation

The product of these successive individual constants is, as before, the over-all basicity constant:

. . . . . . (1.9)

The actual pK values suggest that the two acids H_3X and H_4Y have the structures of betaines (III and IV), for they both behave as dicarboxylic acids with two strongly acidic groups. In the case of NITA the third proton is attached to the nitrogen atom and is not given up until a pH of about 10 is reached. In the case of EDTA there are two ammonium-protons of which the first comes away in a buffer region at pH ~ 6, while the second does not ionise off until pH ~ 10. Infra-red studies of the solid salts suggest an alternative pattern for the ionisation of EDTA since the acid, H_4Y, appears to have four $-COOH$ groups[35]. Successive protons are detached from three of these and a zwitterion structure first appears in the species HY^{-3}.

The composition of the metal complexes of NITA and EDTA can be summarised as follows. With NITA, and when this reagent is in excess, the 1:2 complex of composition MX'^{-6}_2 must be taken into consideration besides the 1:1 complex, MX'^{-3}, which is the most important species. The free-energy change on chelating the second ion of X^{-3}

is, however, very much smaller than that for the formation of the normal 1:1 complex

so the 1:2 complex plays no significant role in complexometry.

In the case of EDTA too, only the 1:1 complexes are of importance. In strongly acid solutions, at pH values below 3, hydrogen-complexes[196] of composition MHY^{-3} are formed. The silver complex, AgY^{-3}, is exceptional for it takes up a proton even at $pH = 6$. In strongly alkaline solutions, on the other hand, hydroxy-complexes of composition $M(OH)Y^{-5}$, $M(OH)_2^{-4}$ appear, not until over $pH = 10$, however, in the case of divalent metals. Mercury is exceptional, for the complex HgY^{-2} is already beginning to transform into the hydroxy-complex $HgY(OH)^{-3}$ by pH ~ 9·1. While the hydrogen-complexes have no special significance, analytically speaking, attention must often be paid to the hydroxy-complexes formed with ter- and tetra-valent metals such as Al, Fe, and Th (and especially in titrations of Type IV, section 2.2.4.) since they are formed even in neutral solution. The formation of 1:2 complexes is only observed with tetravalent ions and has been studied quantitatively in the case of thorium. The tendency to take up a second ion, Y^{-4}, as measured[31] by the stability constant

$$[ThY_2]/[ThY][Y] = 10^{12}$$

is again very small compared with the tendency to form the normal complex[214] where

$$[ThY]/[Th][Y] = 10^{23} \quad .$$

CHAPTER TWO

Basic Theory of Complexometric Titrations

2.1. Complex Formation

The reactions which take place when a solution of a metal cation is admixed with one of a complexing agent cannot, as a rule, be represented simply by equation (2.1)

$$. \quad . \quad . \quad . \quad . \quad (2.1)$$

or the corresponding mass-action expression (1.8), since the free anions X^{-3} and Y^{-4} do not begin to appear in quantity until above $pH = 10$. For example, in a solution neutralised by alkali to $pH = 7$, NITA occurs as the di-alkali metal salt, Na_2HX, (cf. the pK values in Table 2) so that the reaction between a metallic salt and such a solution takes the following course[218]:

$$M^{+\nu} + HX^{-2} \rightarrow MX^{\nu-3} + H^{+} \quad . \quad . \quad . \quad . \quad (2.2)$$

Hence, as the metal complex forms, hydrogen ions are liberated which results in a lowering of the pH which can amount to several pH units if the solutions are unbuffered. The first types of complexometric titrations to be discovered (Type IV, see section 2.2.4. below) were based on such pH-effects[223].

Naturally, the same considerations apply to EDTA and the following equations hold, depending on the pH region used[200]:

$$\text{at pH 7 to 9:} \quad M^{+\nu} + HY^{-3} \rightarrow MY^{\nu-4} + H^{+} \quad . \quad . \quad (2.3)$$

$$[illegible] \quad . \quad (2.4)$$

Thus complex-formation can be described in a general manner by the equation

$$M^{+\nu} + H_jZ^{j-\mu} \rightarrow MZ^{\nu-\mu} + jH^{+} \quad . \quad . \quad . \quad . \quad (2.5)$$

for which the appropriate mass-action expression is

$$K = [MZ][H]^{j}/[M][H_jZ] = K_{MZ}/\kappa_{H_jZ} \quad . \quad . \quad . \quad (2.6)$$

Using equation (2.6), the equilibrium constants of equations (2.2), (2.3), and (2.4) can be calculated from the data of Table 2.

One result of the basicity of the ions X^{-3} and Y^{-4} is that the change in free-energy on forming a complex is a function of pH. A measure of this change in free-energy is provided by the value of the *apparent complex formation constant*, $(K_{MZ'})_H$, appropriate to the particular-hydrogen-ion concentration, H, of the solution. It is defined as

$$(K_{MZ'})_H = [MZ]/[M][Z]'_H \quad . \; . \; . \; . \; (2.7)$$

where $[Z]'_H$ denotes the total concentration, at the specified hydrogen-ion concentration, of the complexing agent that is *not* bound to metal. Thus

$$[Z]'_H = [Z] + [HZ] + [H_2Z] + \ldots = \sum_{j=0}^{J} [H_jZ] = \alpha_H[Z] \quad (2.8)$$

$$\text{where } \alpha_H = 1 + [H]\kappa_{HZ} + [H]^2\kappa_{H_2Z} + [H]^3\kappa_{H_3Z} + \ldots$$

$$= 1 + \sum_{j=1}^{J} [H]^j\kappa_{H_jZ} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (2.9)$$

Finally, a combination of equations (1.8), (2.7) and (2.8) yields the desired apparent formation constant:

$$(K_{MZ'})_H = K_{MZ}/\alpha_H \quad . \; . \; . \; . \; (2.10)$$

The value of the parameter α_H can be calculated from the appropriate pK values of Table 2, and its magnitude for NITA and EDTA is shown as a function of pH in Fig. 2.

2.2. Survey of Different Types of Complexometric Titrations

A distinction can be drawn between the following types of complexometric titrations.

2.2.1. *Type I. Direct Titrations*[12, 211, 223]. A solution of the chelating agent, almost without exception an alkali-metal salt of EDTA, serves as the titrant. The solution to be titrated and containing the metal to be determined is buffered to the desired pH (*e.g.* to pH = 10 with NH_4^+—NH_3) and titrated directly with the standard solution. Since titrations are generally carried out in solutions more alkaline than pH = 7, the hydroxide of the metal to be determined would normally precipitate. Such precipitation is prevented either by the components of the buffer used, *e.g.* by NH_3 when dealing with Ni^{+2}, Cu^{+2}, Zn^{+2}, Cd^{+2}, etc., or some auxiliary complexing agent is added to the buffer mixture, such as tartrate or citrate in the case of *e.g.* Mn^{+2}, Pb^{+2}, In^{+3}, etc., to keep the metals in solution.

The equivalent point in the direct titration is recognised by the fact that as soon as it is reached [M], the magnitude of the concentration of the metal being determined, decreases abruptly. This is generally detected by the change in colour of a metal-indicator which responds to changes in pM in the same way that an acid-base indicator responds to changes in pH. In titrating zinc or ferric ions, a redox indicator can also be used. An amperometric end-point is almost always possible using the diffusion current passing through the solution of the metal cation undergoing titration to a dropping mercury electrode[86, 130, 145, 160, 178, 180]. A potentiometric end-point is possible only where there is an electrode reversible to the metal cation being determined, *e.g.* with Zn, Cd, and Cu where an amalgam of these metals can serve as an electrode. The change of potential at a dropping mercury electrode when the current is held constant has been used as an indicator[3] for the complexometric titration of Ca and Cd. High-frequency conductance measurements have also been used to detect end-points[16, 94, 95].

2.2.2. *Type II. Back-titration*[12]. Back-titration must be adopted when the metal to be determined cannot be kept in solution at the pH need for complex formation, or when there is no suitable metal-indicator for the direct titration. The standard solution of titrant again consists of EDTA and is added until a slight excess is present. After this, the solution is buffered to the desired pH, and finally the excess EDTA is back-titrated with a standard solution of a metal. A solution of $ZnSO_4$ or $MgSO_4$ generally serves for this purpose and the end-point is detected by using the metal-indicator which responds to the metal introduced in the back-titration. Generally speaking, an amperometric end-point is also possible.

2.2.3. *Type III. Substitution Titration*[12]. Instead of carrying out a back-titration, the metal cation, M, to be determined can be treated with the magnesium complex of EDTA when the following reaction takes place:

$$M^{+\nu} + MgY^{-2} \rightarrow MY^{\nu-4} + Mg^{+2} \quad . \quad . \quad . (2.11)$$

This equilibrium lies almost always to the right since the magnesium complex is, as a rule, less stable than that of the complex, $MY^{\nu-4}$ which EDTA forms with the metal to be determined (cf. Table 2). After the displacement has occurred the magnesium ions set free can be titrated with a standard solution of EDTA. Eriochrome Black T turns out to be an especially good indicator for magnesium.

Theoretically, similar substitution titrations should be possible with the complexonates of other metals besides magnesium. To this end the position of equilibrium in equation (2.11) can be displaced by auxiliary complexing agents when it is desired to replace magnesium by, *e.g.* Zn, Cd, or Cu. Thus even the alkaline earth metals can react with the zinc-, cadmium-, or copper-complexes of EDTA if the reaction mixture contains sufficient ammonia; for the heavy metal is taken up by the ammonia to give ammine-complexes with a concurrent reduction in the concentration of free heavy metal ion. For example, in a strongly ammoniacal solution, barium ions can be replaced by zinc ions, and then the latter can be titrated.

$$Ba^{+2} + ZnY^{-2} + 4NH_3 \rightarrow BaY^{-2} + Zn(NH_3)_4^{+2} \quad .(2.12)$$

The position of equilibrium in such a replacement reaction is determined by the apparent formation constants of the two metallic EDTA-complexes, *i.e.* $(K_{M'Y'})_{H,\,A}$, which are defined later in equation (2.22).

2.2.4. *Type IV. Alkalimetric Titration*[223, 211].

2.2.4.1. If, in a replacement reaction like that represented by equation (2.11), the magnesium complex of EDTA were to be replaced by a proton complex, *e.g.* by the ion HY^{-3} or H_2Y^{-2}, reactions represented by equation (2.3) or (2.4) would take place depending on whether the tertiary or secondary alkali metal salt of EDTA had been used. The hydrogen ions thereby set free in stoichieometric quantities can then be titrated with alkali[209] using either a potentiometric end-point, or an acid-alkali indicator. This procedure is specially to be recommended as a preliminary titration when a back-titration (Type II) is to be performed and it is desirable to avoid a large excess of EDTA. The back-titration can be carried out immediately after the alkalimetric titration, and on the same solution, after adding the metal indicator.

2.2.4.2. If it is not proposed to carry out a back-titration but to rely on the titre of NaOH in the alkalimetric determination, the use of NITA in the form of its di-alkali metal salt, Na_2HX, is preferable to that of EDTA. The reaction proceeds according to equation (2.2) and only one titratable proton is produced per atom of metal[207].

2.2.4.3. As with any other acid of sufficient strength, the hydrogen ions liberated according to equation (2.2) can be determined iodometrically. To this end an iodide-iodate mixture is added as well as the complexing agent HX^{-2} to the metal to be determined. Elementary iodine is liberated in proportion to the amount of metal present, thus:

$$M^{+\nu} + HX^{-2} + \tfrac{1}{6}IO_3^- + \tfrac{5}{6}I^- \rightarrow \tfrac{1}{2}H_2O + \tfrac{1}{2}I_2 + MX^{\nu-3} \quad .(2.13)$$

The weak feature of all methods based on Type IV is that the solution of the metal to be determined must be very precisely neutralised before titration starts—which, on account of the hydrolysis of many metal salts, is often a matter of great difficulty. Naturally any excess of acid is included in the titre and leads to erroneous and high results.

2.2.5. *Type V. Special Methods.* Under this heading will be grouped a number of different indirect procedures which are not of general applicability.

2.2.5.1. Titration of the cation of a sparingly soluble salt, in which form the ion to be determined has previously been precipitated.

Thus sodium[57] can be determined by titrating the zinc present in the precipitated triple acetate, $NaZn(UO_2)_3Ac_9$, and phosphate[74] by titrating the magnesium present in $Mg(NH_4)PO_4$.

2.2.5.2. Precipitating the component to be determined with an equivalent amount of a titratable cation.

This principle is used in the determination of sulphate[5]; barium sulphate is precipitated from a known excess of barium ions, and the amount remaining is determined by back-titration with EDTA.

2.2.5.3. Tieing up an equivalent amount of a titratable cation by complexing it with the substance to be determined.

This principle is used in determining cyanide[108]. The solution of CN^- to be determined is treated with an excess of Ni^{+2} whereby $Ni(CN)_4^{-2}$ is formed; the amount of nickel which is not bound up as this complex is then measured by back-titration with EDTA.

2.2.5.4. Exchange reaction between $Ni(CN)_4^{-2}$ and the material to be determined whereby nickel ions, which are readily determined quantitatively, are set free.

Silver[58], palladium[62], and gold, which themselves cannot be titrated complexometrically, can be determined in this way. Thus:

$$Ni(CN)_4^{-2} + Pd^{+2} \rightarrow Pd(CN)_4^{-2} + Ni^{+2}$$

$$Ni(CN)_4^{-2} + 2Ag^{+} \rightarrow 2Ag(CN)_2^{-} + Ni^{+2} \quad . \quad . (2.14)$$

Since these reactions even take place with sparingly soluble silver salts, the halide ions Cl^-, Br^-, I^-, and thiocyanate ions, SCN^-, can be determined by first precipitating them as the silver salt, dissolving this in a solution of $Ni(CN)_4^{-2}$, and determining the equivalent amount of nickel thereby set free.

2.2.6. *Type VI. Further Possibilities.* In the case of manganese a reductometric titration of the Mn(III) complex is possible. The Mn(II) complex of EDTA can be oxidised by lead dioxide to the reddish-violet complex, MnY^-, of tervalent manganese; this can then be reduced quantitatively by titrating it with a standard solution of ferrous sulphate[174]. Instead of reducing the Mn(III) complex, it is also feasible to oxidise the Mn(II) complex[174, 183]. Silver can be titrated with a standard solution of ferrous sulphate after adding EDTA, for under these conditions Fe(II) is able to reduce Ag(I) quantitatively to the form of metal[173].

Methods have been proposed for determining cobalt both by oxidimetry and reductometry in which the cobaltous complex, CoY^{-2}, is transformed into the cobaltic complex, CoY^-, or *vice versa*[184]. A photometric determination of Mn, Cr, and Co, all of which form deep violet-red complexes with EDTA, has been recommended by Přibil[176]. Ni, Cu, and Fe can be determined in analogous ways if light of the appropriate wavelength is employed[156, 158, 157]. Furthermore, a photometric determination of Co with NITA is possible[155].

These reductometric, oxidimetric, and photometric procedures will not be discussed in detail in the present monograph.

2.3. Titration Curves of Complexometry

2.3.1. In direct titrations of Type I (section 2.2.1.) the metal to be determined is present as free aquated ions, $M^{+\nu}$, or in the form of a series of complexes $MA^{\nu-\lambda}$, $MA_2^{\nu-2\lambda}$, $MA_3^{\nu-3\lambda}$, . . . $MA_n^{\nu-n\lambda}$ . . ., up to $MA_N^{\nu-N\lambda}$. Here, $A^{-\lambda}$ refers to the material added to produce a buffering action (*e.g.* ammonia, for which $\lambda = 0$) or to an accessory complexing agent, *e.g.* tartrate, added to prevent the hydroxide of the metal from precipitating. A standard solution of EDTA, usually in the form of its di-sodium salt, Na_2H_2Y, is introduced from a burette whereupon the following reaction takes place:

$$MA_n^{\nu-n\lambda} + H_jY^{j-4} \rightarrow MY^{\nu-4} + jH^+ + nA^{-\lambda} \quad . \quad .(2.15)$$

Although hydrogen ions are set free in this process, the pH is held constant by the addition of a buffer which also serves to determine the particular stage of ionisation of EDTA which takes part in the reaction, *i.e.* it determines the value of j in equation (2.15).

Our task is now to calculate the value of [M] (and thence $pM = -\log_{10}[M]$) as a function of a, the number of gram-molecules of the titrant EDTA added per mole of total metal, $[M]_t$. As before, the subscript t is used to denote the total concentration of any species in all its possible forms. It will be assumed that these total concentrations remain constant throughout a titration, the small dilution caused by the addition of titrant being neglected. We then have for the total concentration of metal:

$$[M]_t = [M]' + [MY] \quad . \quad . \quad . \quad . \quad . \quad .(2.16)$$

where [M]′ denotes the total concentration of metal that is *not* bound to EDTA, so that:

$$[M]' = [M] + [MA] + [MA_2] + \ldots = \sum_{n=0}^{n=N} [MA_n] = \beta_A[M] \quad (2.17)$$

Similarly, the total concentration of EDTA is given by:

$$[Y]_t = a[M]_t = [Y]' + [MY] \quad . \quad . \quad . \quad .(2.18)$$

where [Y]′ denotes the total concentration of EDTA in all its forms that is *not* bound to metal, so that:

$$[Y]' = [Y] + [HY] + [H_2Y] + \ldots \sum_{j=0}^{j=4} [H_jY] = \alpha_H[Y] \quad (2.19)$$

Since the components of the buffer, as well as any accessory complexing agents, are present in great excess compared to $[M]_t$, both [H] and [A] remain constant throughout the titration; in consequence, the two coefficients α_H and β_A are constants for any particular titration. The first of these coefficients can be calculated from the pH of the solution and the known pK values for EDTA using equation (2.9), and in this case:

$$\alpha_H = 1 + \sum_{j=1}^{j=4} [H]^j \kappa_{H_jY} \quad . \quad . \quad . \quad . \quad .(2.20)$$

The second coefficient involves the formation constants for the complexes MA_n:

$$\beta_A = 1 + \sum_{n=1}^{n=N} [A]^j \kappa_{MA_n} \quad . \quad . \quad . \quad . \quad .(2.21)$$

When A = NH_3, the necessary data are given in Table 1. If we now introduce the apparent formation constant for the complex MY, through the definition:

$$(K_{M'Y'})_{H,\,A} = [MY]/[M]'[Y]' = K_{MY}/\alpha_H \cdot \beta_A \quad . \quad .(2.22)$$

we have with (2.16) to (2.22) sufficient equations to calculate the required concentration, [M], from the experimental values $[M]_t$, $[Y]_t$, and *a*.

The results of such calculations are shown in Figs. 4 to 10. A mixture of ammonia and an ammonium salt was always used as the buffer, and the total concentration was held constant such that:

$$[A]_t = [NH_3] + [NH_4^+] = 10^{-1}$$

The auxiliary complexing agent, A, which keeps the metal in solution is therefore ammonia, and its concentration [A] which has to be introduced into equation (2.21) varies with the pH of the solution in the following way:

pH	4	5	6	7	8	9	10	11	12
[A]	5×10^{-7}	5×10^{-6}	5×10^{-5}	5×10^{-3}	0·0048	0·033	0·0833	0·098	0·100

The total concentration of titratable metal was chosen to be $[M]_t = 10^{-3}$, so that the titration curves start at pM = 3 for $a = 0$, provided there is no appreciable complex-formation with the ammonia present. The higher the ammonia concentration, and the greater the stability of the ammine complexes (*i.e.* the larger the value of the constants κ_{MA_n}) the greater the value of β_A according to equation (2.21); in consequence the value of [M] will decrease in accordance with equation (2.17) and a higher value of pM will result before the titration is begun. With the alkaline earth metals, where the formation of ammine complexes need not be taken into account, all the titration curves start at pM = 3. On the other hand, with Zn, Ni, and Cu above pH = 7, the values of pM when $a = 0$ increase with the pH in consequence of the increasing concentration of ammonia in the solution. The rise in pM is greatest with copper since it forms the stablest ammine-complexes (cf. Table 1 and Fig. 3):

It should be noted that [A] does not exceed $[M]_t$ until the pH is greater than 8. Nevertheless, [A] remains constant since NH_4^+ is present in great excess and the pH is fixed, so that the conditions assumed in calculating [M] from equations (2.16) to (2.21) have been met. In practice, of course, pH values below 8 can only be kept constant by supplementing the $NH_4^+ - NH_3$ mixture with another buffer, *e.g.* acetate, appropriate to the desired range of hydrogen ion concentration. In the absence of such additional buffering material the pH would fall during the titration since, according to equation (2.4), hydrogen ions are set free.

Since the constants given in Tables 1 and 2 were used to obtain Figs. 4 to 10, they are strictly valid only for solutions of ionic strength $\mu = 0{\cdot}1$ and a temperature of 20°C. The stability constants for $MY^{\nu-4}$ are somewhat larger at lower ionic strengths[33, 36] and we should obtain titration curves with a bigger break in pM.

The value of pM after passing the end-point ($a > 1$) is determined exclusively by the value of the apparent stability constants given by equation (2.22). The higher the pH, the smaller the value of α_H according to equation (2.20), and the greater the value of $(K_{M'Y'})_{H,A}$. Therefore if an excess of EDTA is present, so that $[Y]_t > [M]_t$, [M] is smaller, the higher the pH. But at pH = 10 the value of α_H has already dropped to 2.6, and with further increases in alkalinity it rapidly approaches its limiting value of unity (cf. equation (2.20) and Fig. 2), so that the extent of the jump in pM at the end-point scarcely increases above pH = 10 provided, as in the case of copper, no hydroxy-complexes, $MY(OH)^{r-5}$, are formed.

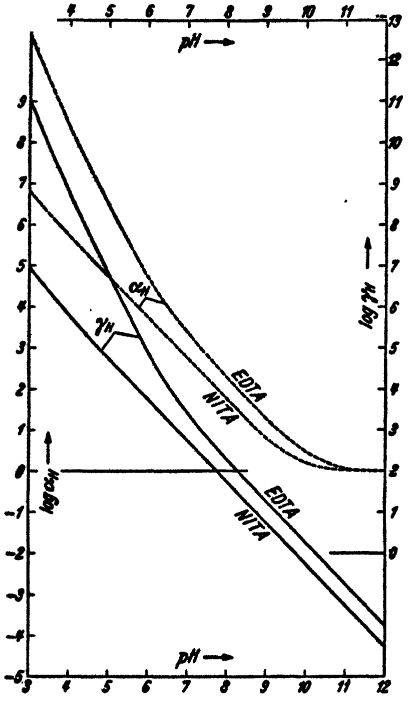


FIG. 2

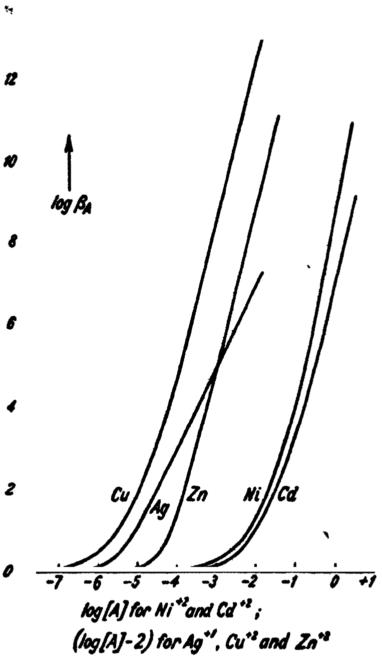


FIG. 3

FIG. 2. The coefficients α_H and γ_H for both NITA and EDTA, shown as a function of pH on a logarithmic scale

FIG. 3. The coefficient β_A (where A = NH_3) shown as a function of ammonia concentration on a logarithmic scale

Figs. 7, 8, and 9 show very clearly how carefully the conditions must be chosen when carrying out complexometric titrations. In order to stabilise the complex formed during the titration as much as possible and to achieve a large break in pM it is advantageous to work at a high pH. But this approach can only be fully exploited with the alkaline-earth metals. With the heavy metals, the basic components of the buffer (*e.g.* NH_3 or OH^-) also form complexes with the metal to be titrated so that the first branch of the titration curve (from $a = 0$ to $a = 1$) is displaced vertically up the pM axis whence the jump in pM occurring at the end-point is made smaller.

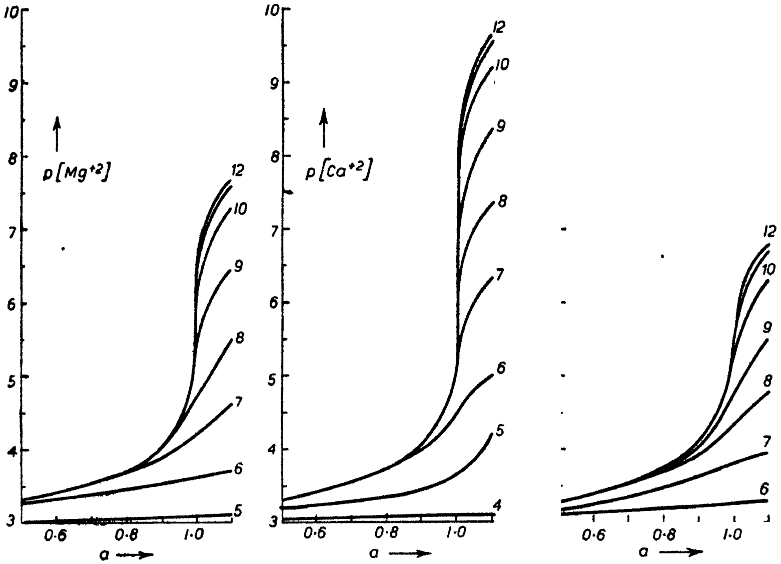


FIG. 4 FIG. 5 FIG. 6

Titration curves for magnesium (Fig. 4), calcium (Fig. 5), and barium (Fig. 6) with ethylenediaminetetra-acetic acid at various pH-values

When raising the pH it will therefore be advantageous to use bases which form as weak complexes as possible with metals. At the same time the metals to be determined must be kept in solution and any precipitation of hydroxides avoided. Quite narrow limits are thus set to the choice of reaction conditions.

The titration curves for Fe(III) have only been calculated for low pH-values since these alone are of importance in practice. The vertical displacement of the branches of the titration curves prior to the end-point for pH = 3 and 4 is to be referred in this instance[216] to the formation of the hydroxy-complex $Fe(OH)^{+2}$, since

There will, of course, be curves analogous to those of Figs. 4–10 for the titration of Cd^{+2}, Pb^{+2}, In^{+3}, Bi^{+3}, Th^{+4}, and of the rare-earth cations, all of which can be titrated according to Type I procedure (section 2.2.1). As yet we are unable to construct them for lack of the necessary formation constants of the complexes MA_n produced by the auxiliary complexing agents such as, *e.g.* tartrate; furthermore, the colour-change curves for these metals with metal-indicators (*e.g.* Erio Chrome Black) have never been investigated quantitatively.

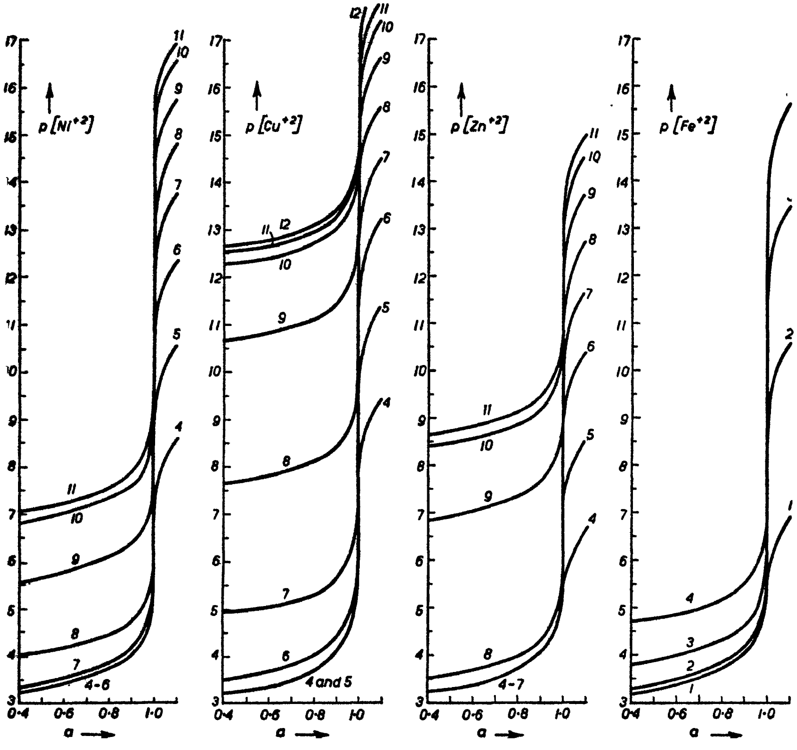


FIG. 7 FIG. 8 FIG. 9 FIG. 10

Titration curves for nickel (Fig. 7), copper (Fig. 8), zinc (Fig. 9), and iron (Fig. 10) with ethylenediaminetetra-acetic acid at various pH-values

2.3.2. Little need be said concerning the titration curves for back-titrations of Type II (section 2.2.2). This type of titration is used particularly for lead and mercury whose complexes with EDTA are appreciably stabler than MgY^{-2} and ZnY^{-2}, the complexonates of the two cations which serve for the back-titration. Thus in the back-titration of the excess of EDTA we retrace quite simply the curves already shown in Figs. 4 and 9, merely in the reversed direction.

2.3.3. With substitution titrations of Type III (section 2.2.3), where the cation to be determined is replaced by Mg^{+2}, we always arrive at simply the titration curve of Mg^{+2} itself (Fig. 4). Since the complex, $MY^{\nu-4}$, of the cation being determined is far stabler than that of the magnesium complex, MgY^{-2}, reaction (2.11) proceeds almost completely to the right, and after the substitution we have only to titrate the Mg^{+2} so formed. A different state of affairs arises when the apparent stability constants of $MY^{\nu-4}$ and MgY^{-2} are of the same order of magnitude. Here we have to deal with a simultaneous titration in which $M^{+\nu}$ and Mg^{+2} are present together in solution in appreciable concentrations and react simultaneously with the EDTA as it is added. This situation is of particular importance with mixtures of the alkaline-earth metals. For example, Ca^{+2} and Mg^{+2} are titrated together when determining the hardness of water[12]. The same problem arises in the substitution titration of calcium, strontium, and barium; because of their importance the simultaneous titrations of Mg and Ca, Mg with Sr, and Mg with Ba are portrayed in Figs. 11, 12, and 13. In order to arrive at these graphs it was necessary to compute, for every value of a during the titration, the concentrations of each of five species, *viz.* [M], the concentration of the free magnesium cation, $[Mg^{+2}]$; $[M^*]$, that of the second alkaline-earth cation; [MY] and $[M^*Y]$, the concentrations of the two complexes with EDTA; and $[Y]'$, the total concentration of the complexing agent *not* bound to either metal. To solve for these five unknowns we have the two apparent formation constants of the species MY and M*Y (as defined by equation 2.22 with $\beta_A = 1$) together with the following three equations:

$$. \quad . \quad . \quad . \quad . \quad (2.23)$$

$$[M^*]_t = [M^*] + [M^*Y] \quad . \quad . \quad . \quad . \quad (2.24)$$

$$[Y]_t = a([M]_t + [M^*]_t) = [Y]' + [MY] + [M^*Y] \quad . (2.25)$$

The calculations were carried out for a constant pH = 10, and it was further assumed that the heavier alkaline-earth metal was present at a constant concentration of $[M^*]_t = 10^{-3}$. Varying amounts of Mg^{+2} are then supposed to be added to the solution of M^* (Ca^{+2}, Sr^{+2}, or Ba^{+2}) and the mixture titrated with EDTA. Since the indicator responds to Mg^{+2}, variations in the value of pMg are the most important aspects of the titration and are shown as continuous lines in Figs. 11 to 14. The concurrent variations in pM* are shown (broken lines) only for the particular case where

It should be noted that with a mixture of Ca + Mg, the calcium is removed from solution first, and then after it has gone the magnesium.

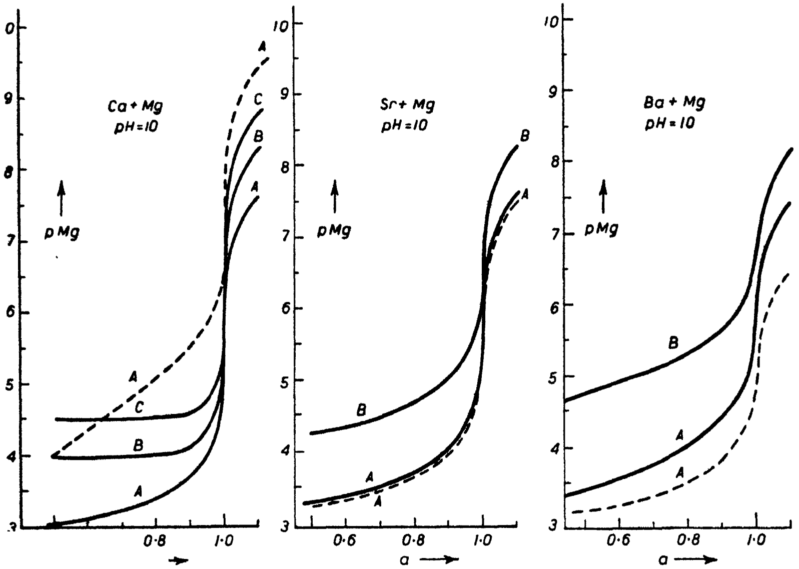


FIG. 11 FIG. 12 FIG. 13

Simultaneous titrations of alkaline-earth metals at pH = 10. Variations in pMg are shown as continuous curves

FIG. 11. In curves A, B, and C, the ratio of calcium to magnesium is 1:1, 10:1, and 100:1. Variations in pCa are shown by the broken curve

FIG. 12. In curves A and B, the ratio of strontium to magnesium is 1:1, and 10:1. pSr shown by broken curve

FIG. 13. In curves A and B, the ratio of barium to magnesium is 1:1, and 10:1. pBa shown by the broken curve

But with a mixture of Sr + Mg the concentrations of the two cations decrease simultaneously, while with a mixture of Ba + Mg, the magnesium is the first to react with EDTA and the barium does not form a complex until afterwards. Such behaviour is naturally determined by the relative values of the respective formation constants (cf. Table 2).

The abscissae in Figs. 11 to 15 show the value of a, the ratio of moles EDTA added during the titration to the total number of moles of alkaline-earth metals (cf. equation (2.25)); when $a = 1$, sufficient complexing agent has been added to combine with both cations.

In a volumetric determination of the hardness of water, the combined concentrations of calcium and magnesium is obtained. This is because the titration is carried out at pH = 10, using a metal-indicator (Eriochrome Black T) which responds to magnesium[12]. As shown in Fig. 11 there is a well-marked jump in pM when $a = 1$, *i.e.* at the point where both metals are bound up as complexes.

Calcium can also be determined in the presence of magnesium by carrying out the titration in a more strongly alkaline solution, at pH $\sim$ 13, for instance. When $a = 0{\cdot}5$, *i.e.* when an amount of EDTA has been added equivalent to the calcium present, there is a small break in pCa (Fig. 14, broken curve I) which can be detected by using the indicator murexide which responds to changes in calcium ion concentration. That the course of the titration curve differs from that shown in Fig. 11 is due to the fact that the hydroxide complex of magnesium[47], $MgOH^+$, is more stable than that of calcium.[10] The formation constants[10, 47] for $MgOH^+$ and $CaOH^+$, *viz.*$K_{MgOH} = 380$, and $K_{CaOH} = 25$, must be introduced into equation (2.21) with the hydroxyl-ion concentration in place of [A].

In constructing the curves labelled I in Fig. 14 it was assumed that no $Mg(OH)_2$ would be precipitated. But the solubility of this hydroxide at pH = 13 is naturally fairly low and the two curves labelled II in Fig. 14 (full lines for pMg, broken lines for pCa) are drawn on the hypothesis that equilibration with the solid phase, $Mg(OH)_2$, is achieved at every stage in the titration. This portrays a state of affairs which would be very favourable for the determination of calcium. It cannot, however, be realised in practice; for when calcium is present, the precipitate of $Mg(OH)_2$ is not pure, for it carries down calcium as well. However, by titrating rapidly in dilute solution it will often be possible to work with supersaturated solutions, and the two curves labelled I in Fig. 14 then represent the behaviour of the system.

As already mentioned in section 2.2.3, it is possible to replace heavy metals, *e.g.* zinc, by alkaline-earth metals although the formation constant for the EDTA complex of zinc is very much larger than that of any alkaline-earth complex. The exchange reaction between ZnY^{-2} and Ca^{+2}, Sr^{+2}, or Ba^{+2} is made feasible by using an auxiliary complexing agent such as ammonia which coordinates with the zinc ion as it is displaced from its complex with EDTA and transforms it into a series of complexes, $ZnA_n^{2-n\lambda}$. If this replacement is to proceed to the right, ($K_{Zn'Y'}$), the apparent formation constant of ZnY^{-2} calculated from equation (2.22) must be smaller than the apparent formation constant of the alkaline-earth complex. This can readily be brought about by making β_A large enough. If, for the sake of example, the zinc in ZnY^{-2} is to be replaced by barium ions, β_A must be of the order 10^9 since the ratio of the stability constants of

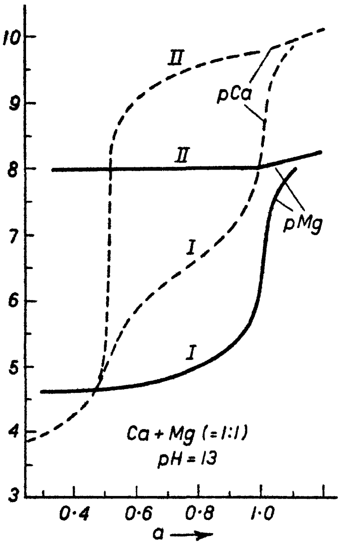


FIG. 14

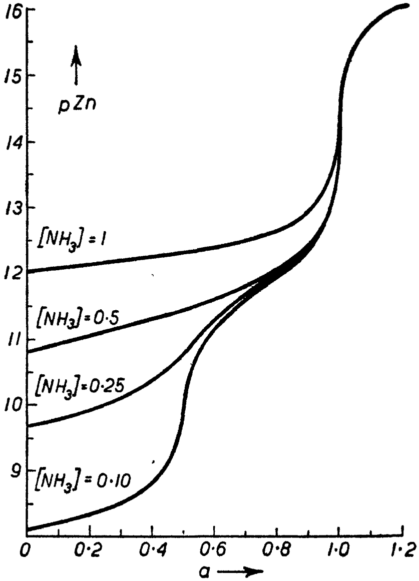


FIG. 15

FIG. 14. Simultaneous titration of Ca and Mg at pH = 13. Full lines represent variations in pMg; broken lines, variations in pCa. The two curves labelled I are calculated on the assumption that no $Mg(OH)_2$ precipitates. Those labelled II are calculated for the case where $Mg(OH)_2$ precipitates, and equilibrium is established with this solid phase

FIG. 15. The curves represent the values of pZn during the simultaneous titration of Ba and Zn at pH = 11 and various concentrations of ammonia. $[Zn]_t = [Ba]_t = 10^{-3}$. It should be noted that when $[NH_3] = 0{\cdot}1$, the two metals react stepwise with EDTA, first the zinc and then the barium. At pH = 10 the curve lies about 0·3 units lower

ZnY^{-2} to BaY^{-2} is $10^{8\cdot 74}$ (cf. Table 2). Further, we can see from Fig. 3 that an ammonia concentration of about 1M is needed in the case of zinc to produce a value of β_A of 10^9. Therefore in about one-molar NH_3, Ba^{+2} and ZnY^{-2} will react smoothly to give BaY^{-2} and $Zn(NH_3)_4{}^{+2}$ according to equation (2.12). To calculate the curves for such a substitution titration, we must obtain pZn and pBa as functions of a; to this end we employ equations (2.23), (2.24), and (2.25) with $M = Ba^{+2}$ and $M^* = Zn^{+2}$ or *vice versa*, in conjunction with the apparent formation constants of ZnY^{-2} and BaY^{-2} calculated from equation (2.22). Fig. 15 shows the results of such calculations for the variation in pZn during the titration of an equimolecular mixture of zinc and barium at pH = 11 and different concentrations of ammonia.

2.3.4. With alkalimetric titrations of Type IV (section 2.2.4) we have to consider how the pH changes as the titrant is added[207, 209, 211].

2.3.4.1. When EDTA is used, an excess of its di-alkali metal salt, Na_2H_2Y, is added to a neutral solution of the metal to be determined[209]. Hydrogen ions are then liberated according to equation (2.4) and these can be determined alkalimetrically using a standard solution of sodium hydroxide. Values of a along the abscissa now represent the number of moles NaOH added per gram atom of the cation being determined. Equations (2.26), (2.27), and (2.28), together with the formation constants of the resulting complexes, $MY^{\nu-4}$, as defined by equation (1.8) permit the calculation of the titration curves. These four relations, *viz.*

$$[M]_t = [M] + [MY] \quad \ldots\ldots (2.26)$$

$$[Y]_t = [Y]' + [MY] \quad \ldots\ldots (2.27)$$

$$[H]_t = 2[Y]_t - a[M]_t = [H] + [H]' - [OH]. \quad \ldots (2.28)$$

$$[MY] = K_{MY}[M][Y] \quad \ldots\ldots (1.8)$$

are sufficient for calculating the concentrations of the four species [M], [MY], [Y]′ and [H]. Once again [Y]′ signifies the total concentration of complexing agent *not* bound to metal. Thus, $[Y]' = \alpha_H[Y]$ (cf. equation (2.19)). By analogy, [H]′ signifies the total concentration of acidic hydrogen that is *not* present as free hydrogen ions; thus

$$[H]' = [HY] + 2[H_2Y] + 3[H_3Y] + 4[H_4Y] \quad \ldots (2.29)$$

Just as [Y]′ is related to [Y] through the coefficient α_H, [H]′ can be related to [Y] through the expression

$$[H]' = \gamma_H[Y] \quad \ldots\ldots (2.30)$$

and the value of the coefficient γ_H can be calculated from the known pK values for EDTA using the relation:

$$\gamma_H = \sum_{j=1}^{4} j[H]^j \kappa_{H_jY} \quad . \quad . \quad . \quad . \quad . \quad (2.31)$$

Numerical values of γ_H calculated from equation (2.31) are shown as a function of pH in Fig. 2. $[H]_t$ is the total concentration of titratable hydrogen, and at the commencement of the titration ($a = 0$) it is equal to $2[Y]_t$ since through using the salt, Na_2H_2Y, two acidic hydrogen atoms are made available by each molecule of EDTA present (cf. equation (2.28)). As a increases, *i.e.* as the amount of NaOH added increases, the concentration of total available hydrogen, $[H]_t$, gets smaller and smaller.

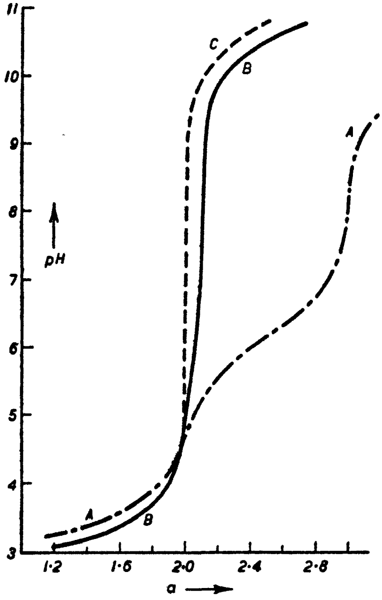


FIG. 16

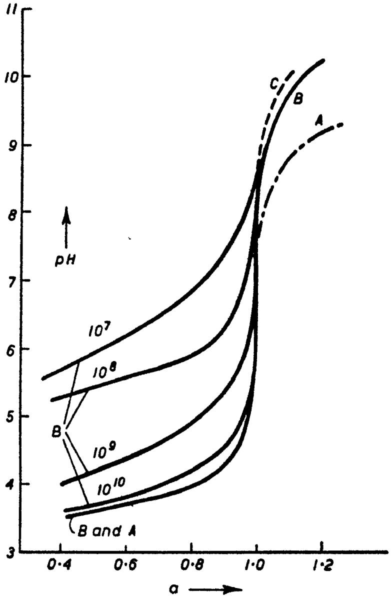


FIG. 17

FIG. 16. Alkalimetric titration of metal cations after adding Na_2H_2Y. Curve A. 100% excess of EDTA. Curve B. 10% of EDTA. Curve C. 0% excess of EDTA

FIG. 17. Alkalimetric titration of metal cations after adding Na_2HX. Curve A. 100% excess of NITA. Curve B. 10% excess of NITA. Curve C. 0% excess of NITA. The figures refer to the formation constants of the complexes of NITA with the metals being titrated

The graphs shown in Fig. 16 have been calculated with the aid of equations (2.26) to (2.31). The three curves start at $a = 0$ just under pH = 3. Since the pH of a solution of Na_2H_2Y is about 5, the decrease in pH brought about by metal-complex formation is about two units. On titrating with alkali, first of all the hydrogen ions liberated in accordance with equation (2.4) are neutralised, a process which produces a small jump in pH at pH = 5 (curve A of Fig. 16). Further addition of NaOH transforms the ion H_2Y^{-2} derived from the excess of EDTA into H_3Y^-. Since $pK_3 = 6{\cdot}16$, the buffer region for this stage of the neutralisation of EDTA is very low down towards the acid side, and the break in pH at $a = 2$ is poorly defined. A very considerable improvement can be made by using the least possible excess of EDTA so that the buffer region at pH 6·16 is shortened (curve B). This point is made very clearly in Fig. 16. Curve A represents a titration in which a two-fold excess of EDTA was used; so that $[Y]_t = 2[M]_t$; curve B, one in which the excess was only 10% ,so that $[Y]_t = 1{\cdot}1[M]_t$; curve C, one in which an equivalent amount of metal and EDTA were taken, so that $[Y]_t = [M]_t$.

The three curves of Fig. 16 are valid for complexes with stability constants greater than 10^{15}. If the formation constant is smaller, reaction (2.4) does not go completely to the right. In consequence, the pH effect is smaller and the branch of the neutralisation curve preceding the point $a = 2$ lies higher up the pH axis, so that the jump in pH at the end-point ($a = 2$) is still further reduced, rendering the procedure of no practical value. Alkalimetric titrations of Type IV can therefore be carried out only with those metals which form the most stable complexes with EDTA. It is just possible to titrate manganese, but not the alkaline-earth metals.

2.3.4.2. The use of HY^-. Titrations of Type IV can also be carried out using the tertiary alkali salt of EDTA, Na_3HY[209]. Reaction (2.3) now replaces (2.4) and titrations of the alkaline earths become feasible. However, the procedure is seldom used, and further details will not be given here.

2.3.4.3. When NITA is used instead of EDTA[207], the procedure is to add an excess of the salt Na_2HX, which has a neutral reaction, to the metal to be determined when reaction (2.2) proceeds. To calculate the course of the titration curves we employ equations analogous to those used for EDTA, *viz.*

$$[M]_t = [M] + [MX] \quad \text{. . . . .(2·32)}$$

$$[X]_t = [X]' + [MX] \quad \text{. . . . .(2.33)}$$

$$[H]_t = [X]_t - a[M]_t = [H] + [H]' - [OH] \quad \text{. .(2.34)}$$

with the additional relations $[X]' = \alpha_H[X]$, and $[H]' = \gamma_H[X]$, in which the coefficients α_H and γ_H can be calculated from the known pK values for NITA (cf. equations (2.20) and (2.31), and Fig. 2). The curves shown in Fig. 17 have been obtained in this way.

The metal complexes formed with NITA are considerably less stable than those with EDTA (Table 2) with the result that the curves of Fig. 17 start at higher pH values. However, the buffer region at pH = 6·16 which had such an unfavourable effect in reducing the pH jump at the end-point of titrations using EDTA (Fig. 16) is absent from titrations using NITA, so that despite the lower stability of its complexes, there is a very good jump in pH at $a = 1$. Even an appreciable excess of Na_2HX has no particularly adverse effect as demonstrated by curve A of Fig. 17 which refers to a two-fold excess of reagent ($[X]_t = 2[M]_t$). However, the end-point is distinctly better in curve B which is calculated for a 10% excess ($[X]_t = 1{\cdot}1[M]_t$). The numbers appended to curves B in Fig. 17 are the stability constants of the corresponding metal complexes. Calculations show that K_{MX} ought to be at least 10^8 for a good end-point and it is therefore still possible to titrate manganese[207]. The method works very well indeed for all the other heavy metals.

Mention must again be made of the fact that all ter- and tetravalent metal cations form hydroxy-complexes and higher complexes as well as the normal 1:1 complexes. These have not been taken into account in equations (2.32) to (2.34), but they will have the effect of making the bend to the right in the neutralisation curves after $a = 1$ take place earlier, so that the jump in pH at the end-point is reduced[207].

CHAPTER THREE

Indicators Used in Complexometry

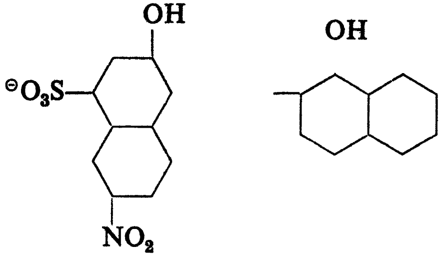
Colour indicators of various kinds are used in complexometric titrations. The most important of these are certain dyestuffs which respond to particular metal cations; these are termed metal-indicators. Conventional pH indicators can be used for titrations of Type IV where the end-point is characterised by an abrupt increase in pH. Finally the end-point can be revealed in a few cases by using oxidation-reduction (redox) indicators.

3.1. Metal Indicators

Molecules of dyestuffs which are able to form complexes with specific metal cations can serve as indicators of pM values. The metal complexes must, of course, have a colour different from that of the dyestuff itself. Generally speaking 1:1 complexes (metal: dyestuff = 1:1) are encountered, but 1:2 complexes (*e.g.* with zinc and Erio T) and 2:1 complexes (*e.g* with calcium and metalphthaleins) also occur.

Like the complexones themselves, the metal-indicators are chelating agents, for it is only through the cooperation of the chelate effect that the metal-dyestuff complex achieves sufficient stability. This implies that the dyestuff molecule possesses several ligand atoms suitably disposed for coordination with a metal atom. These can, of course, equally well take up protons—which also produces a change in colour. Metal-indicators are therefore not only pM but also pH indicators. Furthermore the metal-dyestuff complexes can themselves often take up or lose protons so that we have to take into account a whole range of species in equilibrium with each other, namely the dyestuff and its various proton-complexes, D, HD, H_2D. . ., the metal-dyestuff complex and its different protonated adducts MD, MHD, MH_2D, . . ., and perhaps still higher complexes, MD_2 (1:2), or bimetallic complexes such as M_2D (2:1).

3.1.1. *Eriochrome Black Dyestuffs.* Dyestuffs of this group are derivatives of *o*:*o*′— dihydroxyazonaphthalene (as (V)) and can react with many metals. Of them all, Eriochrome black T (or Erio T, for short) has the most favourable pK values[210]. It possesses the following constitution:*



Eriochrome Black T; (V), H_2D^-.

The sulphonic acid group in the 4-position to the azo-group gives up its proton long before the pH range of 7–12 which is of immediate interest to us here. Only the dissociation of two other hydrogen atoms, namely those of the two phenolic OH groups need therefore be considered and it is appropriate to represent the dyestuff by the abbreviated formula, H_2D^-. The two hydrogen atoms have pK values of 6·3 and 11·55. Below pH = 6 the solution of Erio T is red (due to H_2D^-), between pH 7 and 11 it is blue (due to HD^{-2}), and above pH = 12 a yellowish-orange colour (due to D^{-3}). In the first of these solutions extensive polymerisation to reddish-brown products can be observed and this is one reason why the indicator is not used below pH = 6·5. The other reason is that the metal complexes are also red, so that the addition of metallic salts to an acid solution of this dyestuff produces no clearly defined change in colour.

If on the other hand the pH is between 7 and 11, the addition of metallic salts evokes a brilliant change of colour from blue to red. This can be observed with Mg, Ca, Sc, Y, the lanthanons, Mn, Zn, Cd, Hg, Ga, In, Pb, Al, Fe, Ti, Co, Ni, Cu, and the platinum metals. To keep the pH constant a buffer mixture is added, and most of these metals have to be kept in solution with the aid of weak complexing agents such as ammonia or tartrate. Spectrophotometry has been used for the quantitative investigation of the red metal-dyestuff complexes formed by magnesium[210], calcium[210], and zinc[194]. A single 1:1 complex of the simple formula MD^- is formed by each of these

* Colour Index 203. Schultz-Lehmann, 7th Ed., No. 241. The English equivalent is Solochrome Black WDFA (I.C.I. Dyestuffs). The nitro-group has been shown to be in the 6-position by Ruggli, Zimmermann, and Kapp[190] and not in the 5-position as stated in the Colour Index and Schultz-Lehmann.

two alkaline-earth metals so that the change in colour can be represented by the following equation:

$$M^{+2} + HD^{-2}\,(\text{blue}) \rightarrow H^{+} + MD^{-}\,(\text{red}) \quad . \quad . \quad (3.1)$$

In the case of zinc the 1:2 complex is formed as well as ZnD^{-} so that equation (3.2) succeeds equation (3.1). Thus:

$$MD^{-}\,(\text{red}) + HD^{-2}\,(\text{blue}) \rightarrow MD_2^{-4}\,(\text{red}) + H^{+} \quad . \quad (3.2)$$

The two species ZnD^{-} and ZnD_2^{-4} have practically the same colour, but the molecular extinction coefficient of the higher complex is twice as large since it contains two dyestuff molecules.

Fig. 18 shows the absorption spectra of the species, H_2D, HD, D, and MD, with $M = Mg^{+2}$.

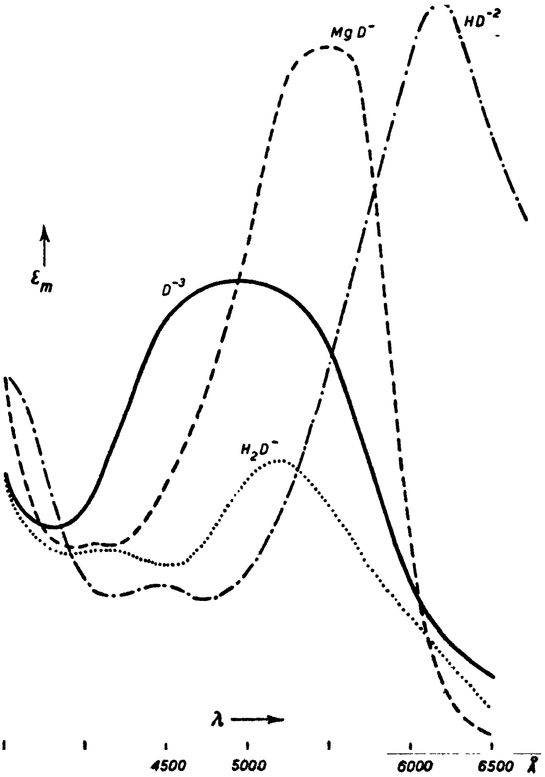


FIG. 18. The absorption spectrum of Erio T at pH ∼ 5 pH ∼ 8 (HD^{-2}), and pH ∼ 13 (D^{-3}), together with that of the magnesium complex (MgD^{-}). ε_m = molecular extinction coefficient. Wavelength (λ) in angstrom units

For analytical purposes it is of primary importance to know the indicator constant defined as follows:

$$= [MD]/[M]\,[D]' \quad . \quad . \quad . \quad . \quad . \quad (3.3)$$

where $[D]' = [D] + [HD] + [H_2D]$ denotes the total concentration of metal-free dyestuff. In the case of zinc we shall also require the formation constant of the higher complex:

$$= [MD_2]/[M]\,[D]'^2 \quad . \quad . \quad . \quad . \quad . \quad (3.4)$$

Since protons are liberated in reactions 3.1 and 3.2, the values of both these indicator constants are dependent upon pH, and this is indicated as before by the suffix H. Table 3 gives some numerical values for these constants.

TABLE 3

Apparent Indicator Constants for $\mu = 0{\cdot}1$ and room temperature

pH	7	8	9	10	11	12
log $(K_1)_H$ for Ca	0·85	1·85	2·85	3·84	4·74	5·27
log $(K_1)_H$ for Mg	2·45	3·45	4·45	5·44	6·34	6·87
log $(K_1)_H$ for Zn	8·4	9·4	10·4	11·4	12·3	
log $(K_2)_H$ for Zn	11·0	13·0	15·0	17·0	18·8	

Using the data from Table 3 we can now construct transition-curves, *i.e.* curves showing how the colour varies with pM. More precisely we are interested in the connection between pM and the shade of colour in various pH regions. Since the concentration term [MD] (or the sum $[MD] + 2[MD_2]$) determines the colour before the complexometric titration is begun, while the concentration term [D]′ is a measure of the colour after the titration, we consider the following ratio:

$$\text{Percentage change in indicator} = 100[D]'/[D]_t \quad . \quad . \quad (3.5)$$

where $[D]_t$ signifies the total concentration of the indicator.

In the case of calcium and magnesium the degree of colour change defined in this way is independent of the total concentration of dyestuff taken, since a combination of (3.3) and 3.5) leads to the following expression:

$$\text{Percentage colour change} = 100/(1 + [M](K_1)_H) \quad . \quad (3.6)$$

If a higher complex is present, equation (3.6) is no longer valid; but a combination of (3.3), (3.4), and (3.5) leads to the more complicated expression:

Percentage change

$$= 100 \times \qquad \qquad (3.7)$$

It should be noted that in this case the percentage change of colour in the indicator used depends on the total concentration $[D]_t$. In practice, however, there is not such a big difference between the two expressions as might appear at first sight; for as a rule the second term under the square root sign is appreciably smaller than the first in which case equations (3.7) and (3.6) become identical.* When considering the colour changes of Erio T with zinc for the case where $[D]_t = 10^{-5}$ (*i.e.* 1% of $[M]_t$), equation (3.7) gives results which differ somewhat from those given by equation (3.6) only at pH = 10 and 11. This indicates that the higher complex, ZnD_2^{-4}, is present only in insignificant amounts when the concentrations of cation and indicator are small.

Figs. 19, 20, and 21 reproduce the results of the calculations.

Among those cations which react with Erio T, Co^{+2}, Ni^{+2}, Cu^{+2}, Al^{+3}, Fe^{+3}, Ti^{+4} and those of the platinum metals form such stable complexes that the dyestuff can no longer be liberated by adding EDTA. Direct titration of these cations using Erio T as the indicator is therefore impracticable. However, with Co, Ni, Cu, and Al a back titration can be carried out, for the rate of reaction of their EDTA complexes, $MY^{\nu-4}$, with the indicator is so slow that it is possible to titrate the excess of EDTA with a standard solution of zinc or magnesium.

Potassium cyanide can be used as a masking reagent for Co, Ni, Cu, and the platinum metals when carrying out a direct titration of other metals using Erio T as indicator[12, 199]. Interference by aluminium or titanium can be suppressed by adding triethanolamine[169], tiron or fluoride[168]. These reagents are ineffective for iron; but if this metal is present only in small amounts, it can be precipitated as sulphide or diethylthiocarbamate, as has been demonstrated, *e.g.* in determining the hardness of ferruginous waters[48]. Where such a treatment is impossible (as in the determination of Pb, Mn, Zn, and Cd which are themselves precipitated by sulphide ions) the iron must be removed before titrating. Admittedly even quite large amounts of iron can be transformed quantitatively into ferrocyanide and so rendered harmless by reducing in acid solution with ascorbic acid and then adding excess of KCN and warming. But so much hydrogen cyanide is set free in the process that it is virtually impracticable for routine analyses.

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* When $b \ll a$, $a^2 + b = (a + b/2a)^2$.

In alkaline solutions, Erio T is very sensitive towards oxidising agents. This explains why this indicator is rapidly discoloured in the presence of manganese or cerium, since these metals are oxidised in alkaline solution even by air, and their oxidation products then attack the Erio T. Addition of ascorbic acid or hydroxylamine prevents these interferences[71].

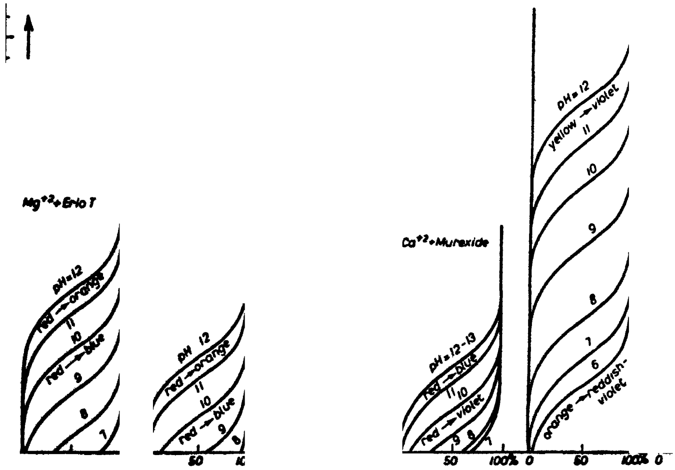


Fig. 19 Fig. 20 Fig. 21 Fig. 23 Fig. 24 Fig. 25

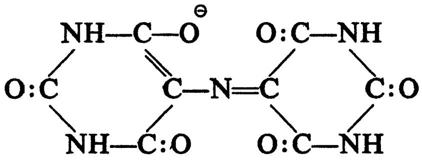
The effect of changes in pH on the colours of various combinations of metals and indicators

Figs. 19, 20, and 21. Eriochrome T with Mg, Ca, and Zn respectively

Figs. 23, 24, and 25. Murexide with Ca, Ni, and Cu respectively

Stock solutions of Erio T in water or alcohol only remain serviceable for a few days[12, 182]. On the other hand a solution in triethanolamine keeps well[49]; some absolute alcohol or concentrated ammonia may be added to reduce the viscosity. The addition of methyl red to the Erio T indicator has also been proposed: the colour then changes during complexometric titrations from red to green thereby improving the visibility of the end-point[84].

3.1.2. *Murexide.* This is the ammonium salt of purpuric acid. Its anion has the following constitution:



Murexide ((VI); H_4D^-)

Solutions of this dyestuff are reddish-violet up to pH = 9; they become violet on further increasing the alkalinity and above pH = 11 are blue-violet[215]. These colour changes must be referred to the progressive displacement of protons from the imido groups[90]. Since there are four such groups it is convenient to represent murexide by the shortened formula H_4D^-. However, only two of these four acidic hydrogens can be removed by adding an alkaline hydroxide[215] so that only two pK values need be taken into account. These are $pK_4 = 9{\cdot}20$ for the process $H_4D^- \rightarrow H_3D^{-2}$, and $pK_3 = 10{\cdot}50$ for the process $H_3D^{-2} \rightarrow H_2D^{-3}$. The anion H_4D^- can also take up a proton to yield free purpuric acid[215] which is yellow in colour and very prone to hydrolysis. However, this requires a hydrogen-ion concentration of about 1 (pH $\sim$ 0).

Murexide reacts with very many metal cations using the central nitrogen atom and the oxygens of the carbonyl groups as ligand atoms[90, 215]. But only in the case of calcium, nickel, cobalt, copper and the rare-earths are the resulting complexes sufficiently stable to find application in analysis. Their colours are red (calcium), orange (copper), or pure yellow (nickel, cobalt) and vary, moreover, with pH just as in the case of the metal-free dyestuff. Hence not only murexide itself but its metal complexes can act as pH indicators since here again a smaller or greater number of protons can become attached to the imido-groups.

Fig. 22 gives the absorption spectra of the ionised species H_4D^- and H_2D^{-3} together with those of the two complexes CaH_2D^- and CuH_2D^-. Since we are concerned exclusively with 1:1 complexes, the general formula $MH_\nu D^{\nu+\nu-5}$ is applicable. With calcium[215] and nickel[194], for example, the species MH_4D^+, MH_3D, and MH_2D^- are encountered in the equilibrium mixtures. In a strongly alkaline solution the copper complex can lose even the two remaining protons[194] and change over to MHD^{-2} and MD^{-3}. The formation of complexes with murexide must therefore be represented by equation (3.8):

$$M^{+\nu} + H_jD^{j-5} \rightarrow MH_yD^{\nu+y-5} + (j-y)H^+ \quad . \quad . \quad (3.8)$$

where j can assume the values 2, 3, or 4, and y the values 0, 1, 2, 3, or 4.

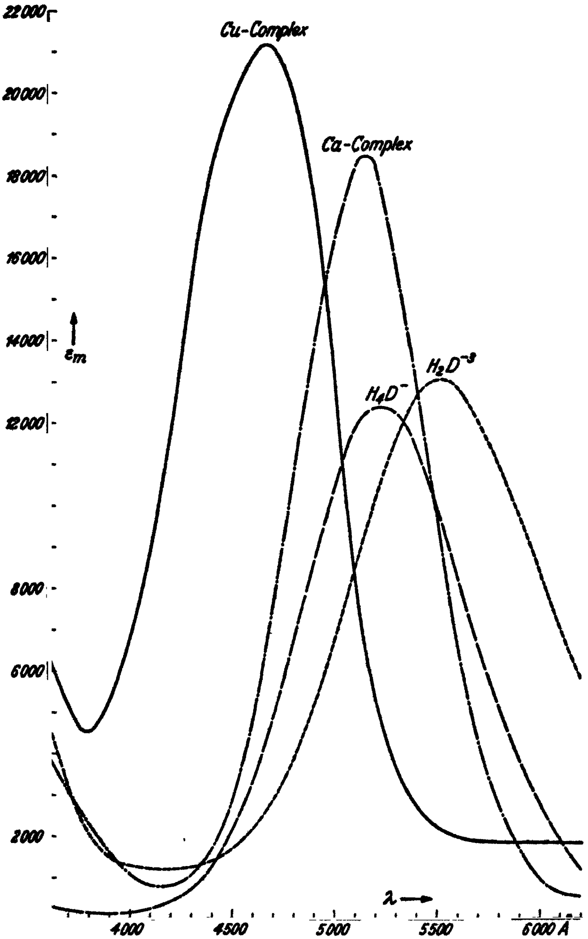


FIG. 22. The absorption spectrum of murexide in neutral solution (H_4D^-) and in strongly alkaline solution (H_2D^{-3}) together with that of the calcium complex at pH = 13 (CaH_2D^-), and that of the copper complex at pH = 8 (CuH_2D^-). ε_m = molecular extinction coefficient; wavelength (λ) in angstrom units

The following equation defines the indicator constants

. . . . . . (3.9)

where [MD]′ denotes the sum of the concentrations of all the metal complexes and [D]′ the sum of the concentrations of all the dyestuff species which contain no metal. Thus:

$$[\mathrm{MD}]' = \sum_{y=0}^{4} [\mathrm{MH}_y\mathrm{D}] \quad \text{and} \quad [\mathrm{D}]' = \sum_{j=2}^{4} [\mathrm{H}_j\mathrm{D}] \quad .(3.10)$$

Since their magnitudes are naturally a function of pH, the indicator constants defined by equation (3.9) are of course characterised as in previous cases by the subscript H. They can be calculated from the pK values of murexide and those of its metal complexes so that with the aid of a few measurements in a narrow pH range, indicator constants for the whole range of hydrogen-ion concentrations become available[194, 215]. The data of Table 4 were obtained in this way and with their help Figs. 23, 24, and 25 were constructed using equation (3.6) but with the constants $(K_j)_\mathrm{H}$ in place of

TABLE 4

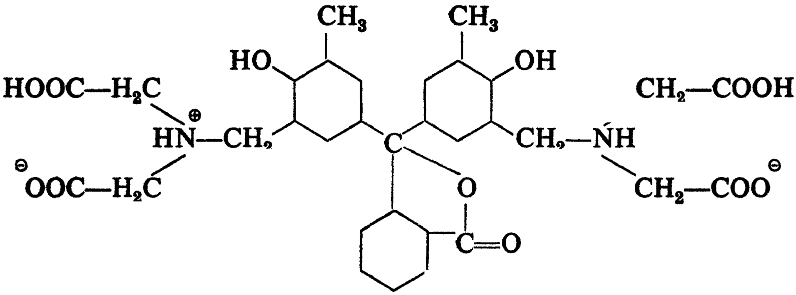
Apparent Indicator Constants for $\mu = 0{\cdot}1$ and room temperature

pH	4	5	6	7	8	9	10	11	12	13
log $(K_j)_\mathrm{H}$ for Ca	2·4	2·6	2·6	2·6	2·8	3·4	4·0	4·6	5·0	5·0
log $(K_j)_\mathrm{H}$ for Ni	4·6	4·6	4·6	5·2	6·2	7·8	9·3	10·3	11·3	—
log $(K_j)_\mathrm{H}$ for Cu	—	5·0	6·4	8·2	10·2	12·2	13·6	15·8	17·9	—

Metal complexes of such extremely high stability that they cannot again be broken up by EDTA are not formed by murexide and, in consequence, titrations with this indicator are less subject to interference by metallic impurities than is the case with Erio T. Addition of triethanolamine[167] will prevent interference caused by the precipitation of Al, Ti, Fe, and Mn when titrating nickel in the presence of ammonia. However, this masking agent cannot be used in the corresponding titration of copper since it forms too stable a complex with cupric ions and partially displaces it from its complex with murexide. Triethanolamine also serves as a masking agent for Fe(III) and Mn in the titration of calcium in strongly alkaline solution[167];in this case Al does not interfere since it is present as aluminate. Fluoride is suitable for masking calcium when titrating copper and nickel. Nickel can also be determined in the presence of copper if Cu(II) is reduced with ascorbic acid to Cu(I) before the ammonia is added.

A saturated solution of murexide has just the right concentration to serve as a stock solution. Unfortunately such solutions only keep from 1 to 2 days[28] and it is, therefore, often preferable to dilute the indicator with solid common salt and to add the finely powdered solid mixture to the liquid to be titrated[67]. For the determination of the purity of a murexide preparation cf. reference 150.

3.1.3. *Metalphthalein.* This is the name given to the compound of constitution (VII) which is a derivative of phenolphthalein and can combine with metals, the process being signalised by a change of colour.



Metalphthalein. ((VII); H_2D)

Since this compound possesses six acidic hydrogen atoms, the shortened formula H_6D will be used. Of the corresponding pK values two, namely pK_5 and pK_6, which refer to the ionisation of the two carboxyl groups, are less than 3. The next two protons are derived from the two phenolic hydroxyl groups and come off in the region of neutrality ($pK_4 = 7$, and $pK_3 = 7{\cdot}8$). Finally the two immonium groups are only very weakly acidic with $pK_2 = 11{\cdot}4$ and $pK_1 = 12{\cdot}0$.

The ability to combine with metals is naturally derived from the two iminodiacetic acid residues, just as in the complexones themselves. The metal cation simultaneously employs the phenolic oxygen atoms as ligands. Above pH = 9, in the region which alone is of interest to us here, two 1:1 complexes, *viz.* MD^{-4} and MHD^{-3}, and also a bimetallic species, M_2D^{-2}, must be taken into account[5].

The metal-free and the complex species are either colourless, pink, or red. The absorption spectra of all the coloured species have the same general form with a single band at $\lambda_{max} = 580$ mμ in the visible, as shown in Fig. 26. The different forms are distinguished solely by the intensity of this band. Numerical data are given in Table 5 where the second and fourth row of figures record ε_{max},

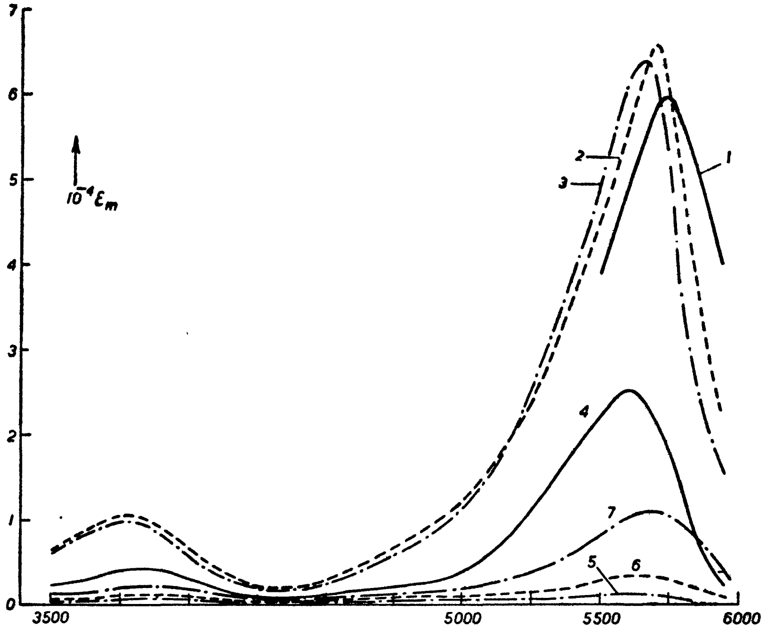


FIG. 26. The absorption spectra of different ionised species and metal complexes derived from the metalphthalein (VII). D^{-6} (Curve 1); Ba_2D^{-2} (Curve 2); Ca_2D^{-2} (Curve 3); Mg_2D^{-2} (Curve 4); Zn_2D^{-2} (Curve 5); H_2D^{-4} (Curve 6); ε_m = molecular extinction coefficient. Wavelength (λ) in angstrom units

the molecular extinction coefficient at the wavelength of maximum absorption[5].

It can be seen from this Table that the ionisation states from H_6D to H_3D^{-3} make no contribution to the optical absorption. Therefore

TABLE 5

Molecular and relative extinction coefficients of the proton- and metal-complexes of the metalphthalein (VII) at λ = 580 mμ

Species	H_4D^{-2}	H_3D^{-3}	H_2D^{-4}	HD^{-5}	D^{-6}	Zn_2D^{-2}	Mg_2D^{-2}
$10^{-5}\varepsilon_m$	0	0	0·04	0·12	0·62	0·01	0·25
Percentage	0	0	7	20	100	2	40

Species	Ca_2D^{-2}	CaD^{-4}	$CaHD^{-3}$	Ba_2D^{-2}	BaD^{-4}	$BaHD^{-3}$
$10^{-5}\varepsilon_m$	0·62	0·62	0·12	0·62	0·62	0·12
Percentage	100	100	20	100	100	20

the indicator remains colourless up to pH = 7 when a pink colour begins to develop since the species H_2D^{-4} begins to be formed in this pH region (cf. the pK values above). The intensity of absorption does not begin to increase again until pH = 11 when the solution becomes dark red since the species HD^{-5} and D^{-6} are formed in rapid succession. Denoting this maximum intensity of colour as 100%, the relative intensities for the other species are given in the third and sixth rows of Table 5.

Of the metal complexes formed by the metalphthalein (VII), only those of the alkaline-earths are strongly coloured. The complexes of the heavy metals are colourless or almost colourless as shown in Table 5 for the case of the zinc complex. Among the alkaline-earth complexes the species MD^{-4} and M_2D^{-2} (M = Ca, Sr, or Ba) attain practically the maximum depth of colour shown by the ion D^{-6}, *i.e.* 100%. Consequently the metalphthalein (VII) is pre-eminently an indicator for the heavy alkaline-earths. It is less suitable for the titration of magnesium, and quite useless for the heavy metals.

In order to estimate the colour changes which are to be expected in the complexometric titration of alkaline-earths, the stability constants of the species M_2D^{-2}, MD^{-4}, and MHD^{-3} are needed for each of these metals[5]. From the values given in Table 6 it will be seen that the normal complexes, MD^{-4}, of Ca and Ba are weaker by some two logarithmic units than the corresponding complexes with EDTA.

TABLE 6

Stability constants of metalphthalein complexes at $\mu = 0{\cdot}1$

Complex	MD^{-4}	M_2D^{-2}	MHD^{-3}	HD^{-5}	H_2D^{-4}
log K for M = Mg	8·9	5·2	7·5	12·0	11·4
log K for M = Ca	7·8	5·0	6·4	12·0	11·4
log K for M = Ba	6·2	3·0	4·8	12·0	11·4

Reading from left to right, the stability constants referred to in Table 6 have the following significance:

$$K = \frac{[MD]}{[M][D]}; = \frac{[M_2D]}{[M][MD]}; = \frac{[MHD]}{[M][HD]}; = \frac{[HD]}{[H][D]}; = \frac{[H_2D]}{[H][HD]}$$

The two last constants refer to the last two pK values of the metalphthalein (VII) and have been quoted earlier on.

If we add the indicator (VII) to a solution of an alkaline-earth at a pH between 9 and 12, the three complex species MD^{-4}, M_2D^{-2}, and MHD^{-3} are formed in amounts depending on the concentration of free metal ions, [M], and on the pH. If such a solution is then titrated with EDTA, the species M_2D^{-2} disappears first, and then MD^{-4} and MHD^{-3} disappear simultaneously provided the pH is held constant.

The figures given in Table 6 naturally permit the relative concentrations of all the coloured species to be calculated for every value of [M] and [H], and in conjunction with the molecular extinction coefficients given in Table 5 the optical absorbancy can be calculated, or rather the intensity of the red coloration expressed as a percentage of the maximum, *viz.* that achieved when all the indicator is in the form D^{-6}. The results of these calculations are reproduced graphically in Figs. 27 and 28.

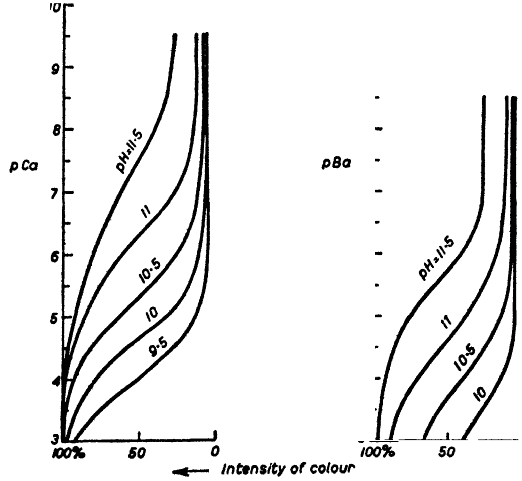


FIG. 27 FIG. 28

The effect of pH on the intensity of coloration of metalphthalein at different values of pCa (Fig. 27) and pBa (Fig. 28)

With calcium at a concentration $[Ca] = 10^{-8}$ the maximum intensity of colour (100%) is reached above pH = 10. As pCa increases the absorbancy decreases; but it never falls to zero even at very high values of pCa, *i.e.* when the calcium ion has practically disappeared. This means that the solution is not completely colourless at the end-point of a titration owing to the presence of the metal-free species H_2D^{-4}, HD^{-5}, and D^{-6}, which have an appreciable absorbancy (Table 5). The same behaviour is observed with barium though here the full colour intensity of 100% is never achieved even at high metal concentrations.

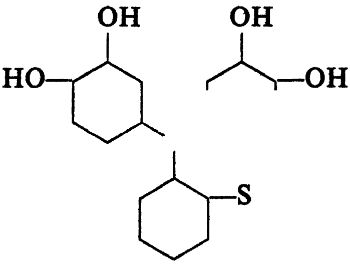
The phthalein indicator (VII) is only slightly sensitive to traces of metallic impurities. The heavy metals can be masked with cyanide, while others precipitate out at the high pH used for the titration. A somewhat unsatisfactory feature is the residual red colour at the end of the titration; but this can be compensated by adding a complementary colour, *e.g.* naphthol green. The stock solution contains the metalphthalein in ammoniacal solution together with the green dyestuff; it is stable for several weeks.

3.1.4. *Tiron.* Tiron[224] is the di-sodium salt of pyrocatechol-3:5-disulphonic acid. It is also used for the absorptiometric determination of titanium and iron, whence its name (Ti-iron). The colourless salt is easily soluble in water and with Fe^{3+} gives a blue 1:1 complex between $pH = 1$ and $pH = 4$, a violet coloured 1:2 complex between $pH = 5$ and $pH = 7$, and above $pH = 7$ a reddish-orange compound with 3 mols. of Tiron per atom of iron[224]. The complexometric titration with EDTA must be carried out in acid solution, for it is only then that the complexone can abstract metal from its complex with Tiron. Since the 1:1 complex is formed under these conditions, equation (3.6) is valid. The relevant values for the indicator constants, $(K_i)_H$, turn out to be very favourable[224] so that curves derived from equation (3.6) for the percentage of colour change during titration coincide with the steep portion of the titration curves shown in Fig. 10. Unfortunately this favourable situation cannot be fully exploited, for the colour of the iron complex is too feeble (molecular extinction coefficient $\sim$ 1,500). A high concentration of indicator must therefore be added ($[D]_t \sim [M]_t$), to ensure that as much as possible of the iron not bound to EDTA before the end-point should be present as the iron-indicator complex. Hence on approaching the end-point there is a gradual paling of the blue colour which disappears completely at the end-point. Unfortunately, the precise observation of this point is somewhat marred by the yellow colour of the EDTA-complex, FeY^-.

Stock solutions of Tiron in water keep well. The behaviour of salicylic acid and thiosalicylic acid as indicators[4] is almost identical (cf. section 3.1.6).

3.1.5. *Pyrocatechol Violet.* Possessing as it does two hydroxyl groups ortho to one another, pyrocatechol is an excellent chelating agent for many metal cations[225]. With the exception of iron, which displays its usual reaction towards a phenol, complex formation is unaccompanied by any visible change in colour. When, however, this reactive grouping of two adjacent hydroxy groups is incorporated as a chromophore into the structure of a dyestuff, the situation is completely changed. This is the case with the following sulphonphthalein (VIII) which has been recommended for complexometric titrations by Přibil and his co-workers[138, 139, 247].

Let us first consider the sequence of colour changes which occur as the pH is altered. A solution of the dyestuff is very strongly acid



Pyrocatechol violet ((VIII); H_4D)

and contains the violet coloured zwitterion, H_4D, with the constitution shown above (VIII). Even at pH ~ 1 there is a change in colour to yellow caused by the loss of a proton from one of the hydroxyl groups para to the central carbon atom ($H_4D \rightarrow H_3D^-$). The indicator remains yellow between pH = 2 and 6 and then at pH = 7 there is a new transition, once again to violet; this is due to the loss of a proton from the second para hydroxyl group ($H_3D^- \rightarrow H_2D^{-2}$). Finally the colour turns blue above pH = 10 in consequence of the ionisation of further hydroxyl groups ($H_2D^{-2} \rightarrow HD^{-3} \rightarrow D^{-4}$). These blue, strongly alkaline solutions are very unstable, however, and lose their colour pretty quickly, probably on account of aerial oxidation.

The complexes of pyrocatechol violet (VIII) with metals are blue too, but whether they all form 1:1 complexes, or admixtures with other species has not yet been established. The stablest of the blue complexes are already formed in the pH range 2 to 6 so that there is a brilliant change in colour from yellow to blue when the appropriate metal cations are added to the indicator solution. This is the case with Bi^{+3} and Th^{+4} which can be determined very satisfactorily by complexometric titration. Complexes of Al^{+3} and Ti^{+4} also form in acid solution, but unfortunately the change in coloration is slow in these cases and the end-point is unsatisfactory.

Complexes of the indicator (VIII) with divalent ions such as Ni^{+2}, Co^{+2}, Cu^{+2}, Zn^{+2}, and Cd^{+2} do not form until the pH is above 7 so that on adding metal to indicator there is only a change from violet to blue which is less readily detectable than the colour change of Erio T or murexide with these metals. The titration of these metals with pyrocatechol violet (VIII) has been described by Czech authors[137].

Fig. 29 shows the absorption spectra of pyrocatechol sulphonphthalein (VIII) in various states of ionisation, *viz.* H_4D (in concentrated hydrochloric acid), H_3D^- (in an acetate buffer) and H_2D^{-2} (in an $NH_3 - NH_4^+$ buffer of pH ~ 8·5). The absorption spectrum of the bismuth-indicator complex (at pH ~ 3) is also shown in Fig. 29; this is probably a bimetallic species M_2D^{+2}. However, this indicator has not yet been fully investigated quantitatively and the stability constants of its metal complexes are still unknown.

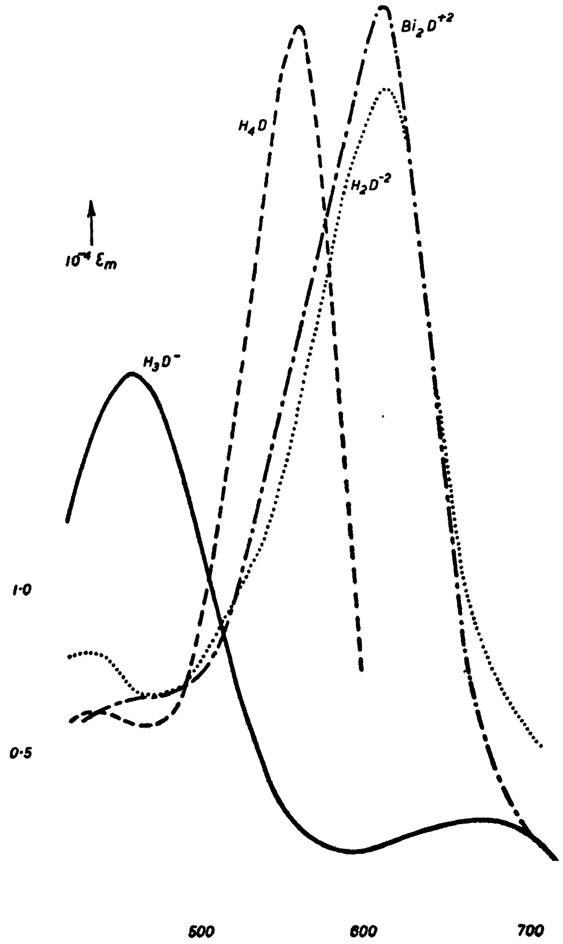


FIG. 29. The absorption spectrum of pyrocatechol violet (VIII) in strongly acid solution (pH < O), in weakly acid solution (pH ~ 5), and in weakly alkaline solution (pH ~ 8), together with the spectrum of the bismuth complex, Bi_2D^{+2}. Wavelengths in millimicrons.

The stock solution of this indicator is prepared by dissolving pyrocatechol violet in water. Such solutions are stable for several weeks.

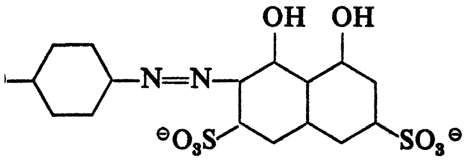
3.1.6. *Additional Metal Indicators.* A number of other processes involving colour changes can be used to indicate the end-point in complexometric titrations.

3.1.6.1. Bismuth ions can be transformed into BiI_4^- by adding an excess of iodide and the deep yellow colour of this complex disappears again when all the bismuth has combined with EDTA. A pH of 2 is suitable for this titration[87, 199]. Thiourea can also be used as an indicator for the titration of Bi[81].

3.1.6.2. Thiocyanate ions can be used as an indicator for Co^{+2} and Fe^{+3}. An acetate buffer is chosen for the former, and a pH of about 2 for ferric iron. In both cases the titration should be carried out in 50% acetone solution[80, 199].

3.1.6.3. Salicylic acid sulphonic acid can be used in place of Tiron as an indicator for iron. Here too the intensity of the colour of the complex is rather low, and the colour changes are less easy to follow with the red salicylic acid complex than with the blue Tiron complex. Salicylic acid itself has been recommended for the complexometric titration of iron[147, 148]. For the composition and stability of these iron complexes see ref. 4.

3.1.6.4. Alizarinsulphonic acid can be used instead of pyrocatechol violet (VIII) for the titration of thorium. Chromotrope 10B, which has the following constitution, is even better suited for this purpose[204].



Chromotrope 10 B (IX)

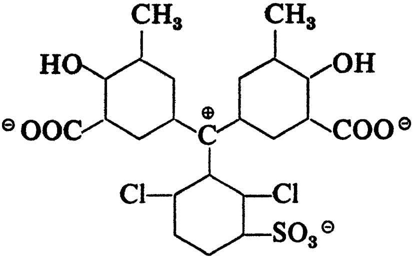
3.1.6.5. Haematoxylin has been recommended for the titration of aluminium[239].

3.1.6.6. Eriochromazurol (Chromazurol S) (X), which has the constitution shown overleaf, has been used for the titration of iron and aluminium[242, 241, 231].

3.1.6.7. In the determination of aluminium, dithizone can serve as an indicator for the zinc used in backtitrating the excess of EDTA[248].

3.1.6.8. Morin can be used for the titration of gallium and indium[159].

3.1.6.9. Eriochromecyanine R has been recommended for the titration of aluminium.



Eriochromazurol (X)

3.1.6.10. 1-(2-Pyridylazo)-2-naphthol is suitable for the titration of zinc, copper, cadmium, and indium[264, 265].

3.1.6.11. "Zincon" (2-carboxy-2′-hydroxy-5′-sulphoformazylbenzene) can be used for the titration of zinc[280].

3.2. Indicators sensitive to changes in Hydrogen Ion Concentration

Ordinary acid-base indicators are needed for titrations of Type IV where the procedure is to measure volumetrically the concentration of hydrogen ions equivalent to the metal to be determined and set free when complex formation occurs in accordance with reactions (2.2) or (2.4).

3.2.1. *Methyl Red—Bromocresol Green.* When working with EDTA there is only a small jump in pH at the end-point (at pH = 4·8, cf. Fig. 16) to be detected by the indicator and a mixture of methyl red and bromocresol green in the proportions 2:3 by weight has proved to be the most suitable. A dilute solution of this mixture is rose-coloured just before the end-point and turns pale blue when it is overshot. Exactly at the end-point, at pH ~ 5, the colour is grey, and this intermediate stage is fairly easy to recognise.

3.2.2. *Methyl Red.* When carrying out titrations of Type IV with NITA, the end-point is characterised by an abrupt change in pH from 6 to 8, as shown in Fig. 17. Now before the complexone, NITA, is added, care must be taken to bring the pH of the solution of the metal cation that is to be determined to the same value as it will have at the end-point of the subsequent titration with standard alkali. Because of the danger of forming a hydroxy-complex, MOH^+, or even of precipitating a hydroxide, $M(OH)_2$, it is impossible in practice to take this preliminary neutralisation much above $pH = 6$. For these reasons a solution of methyl red alone proves the most suitable indicator since at $pH = 6$ it has lost the last trace of its red hue and become a pure yellow.

3.3. Redox Indicators

3.3.1. *Variamine Blue.* When a mixture of ferrous and ferric iron is titrated with EDTA, the trivalent ion disappears first. As soon as a quantity of complexing agent equivalent to the concentration of ferric ion has been added, pFe(III) increases abruptly[216] as shown in Fig. 10. Consequently there is a sudden decrease in the redox potential[179] so that this end-point can also be detected with an oxidation-reduction indicator[65].

It is best to work at $pH \sim 3$. At this acidity the divalent iron remains in solution as the free cation Fe^{+2} even after a distinct excess of EDTA has been added. This is because, according to equation (2.22), the apparent stability constant of the Fe(II) complex, FeY^{-2}, is 10^4 (α_H is about $10^{10\cdot6}$ at $pH = 3$, and K_{FeY} is $10^{14\cdot3}$ from Table 2; β_A is naturally set equal to unity as there is no auxiliary complexing agent present). Then for the redox potential immediately before the end-point we have:

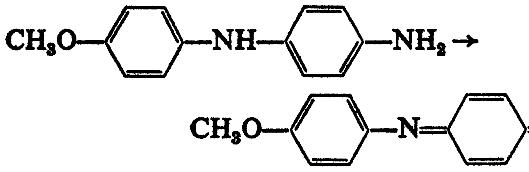
$$E = E^0 + s. \log 10^{-6}/[Fe^{+2}]$$

and immediately after the end-point:

$$E = E^0 + s. \log 10^{-12}/[Fe^{+2}] \quad . \quad . \quad . \quad (3.11)$$

The two values 10^{-6} and 10^{-12} are the concentrations of free ferric iron taken from Fig. 10; E° is the redox potential Fe^{+3}/Fe^{+2} which amounts to about 0·74 volts (relative to the standard hydrogen electrode); the factor s is about 0·06 volts. According then to equation (3.11), the redox potential will decrease at the end-point by about 360 millivolts; furthermore the potential break will be almost independent of the concentration of ferrous iron present. The jump in redox potential will also be obtained even if no ferrous salt is actually added, for the extremely small amounts necessary are present anyway even in practically pure ferric salts. The sharp change in redox potential can be detected very beautifully with a bright platinum electrode and Přibil has used it to indicate the end-point in the potentiometric determination of ferric iron[179].

According to Flaschka[51], variamine blue B is the best indicator for detecting the change of redox potential colorimetrically. The colourless leuco-form is 4-amino-4′-methoxydiphenylamine (XI) which passes on oxidation into O-methylated phenol blue (XII):



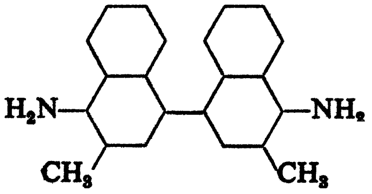
. . (3.12)

(XI) Variamine blue B (XII)

When titrating ferric iron a pH of about 3 is chosen and the colourless hydrochloride of the leuco-base is introduced, whereupon oxidation to the strongly coloured indamine (XII) proceeds with the formation of an equivalent amount of ferrous iron. The ferric iron is now titrated with EDTA and at the end-point the small amount of ferrous iron formed when the indicator was introduced is also transformed into the ferric complex, FeY^-, whereupon the indamine is reduced back to the leuco-base (XI).

The redox potential of variamine blue is 0·60 volts at pH $\sim$ 2, and decreases as the pH rises[51]. The most favourable range of redox potentials for the indicator reaction (3.12) would be a redox potential of about $+$ 0·57 volts. That of the indicator indophenol, which is structurally related to variamine blue, is about $+$ 0·50 volts at pH $=$ 3, *i.e.* it is somewhat too small, and in fact it proves to be not so good for the complexometric titration of iron.

3.3.2. *Dimethylnaphthidine.* With zinc too, a redox indicator can be used to show the end-point in a complexometric titration. To make this possible a very small amount of ferricyanide ion, $Fe(CN)_6^{-4}$, is added. This naturally contains a trace of ferrocyanide ions, $Fe(CN)_6^{-4}$, which combines with the zinc without, however, forming a visible precipitate. The redox potential of the system is therefore relatively high and the indicator, 3:3′-dimethylnaphthidine (XIII), is taken past its transition point.



Dimethylnaphthidine (XIII)

The oxidised form has a beautiful reddish-violet colour[28]. On titrating with EDTA, free zinc ions disappear from the solution as shown in Fig. 9. It is best to work at $pH = 5$ where the value of pZn jumps from 5 to 7 at the end-point. Because of this the metal is removed from the zinc ferrocyanide thereby giving rise again to free ferrocyanide ions; this effects a reduction in the redox potential so that the oxidation product of the naphthidine is reduced back and the violet colour vanishes.

3.4. Absorptiometric Determination of End-points without the Use of Organic Indicators

As Sweetser and Bricker have shown, it is possible to determine the end-point in complexometric titrations without using any supplementary colour indicators[237, 238]. The absorbancy (optical density) is measured at about 225 mμ, for at this wavelength the optical absorption of the two ions, HY^{-3} and Y^{-4}, is still strong whereas their complexes with Mg, Zn, Cd, and Ca show virtually no absorption. However the ion H_2Y^{-2} has much the same absorption characteristics as these metal complexes so that an absorptiometric end-point can only be used when the titrations are carried out in alkaline solution.

Finally, metal cations which absorb light strongly can serve as their own indicators. Thus the end-point in the titration of Fe^{+3} or Bi^{+3} can be determined with the aid of cupric ions[244, 245], for as soon as all the iron (or bismuth) has been bound into its complex with EDTA, there is a change in optical absorption due to the formation from Cu^{+2} of its EDTA-complex, CuY^{-2}.

CHAPTER FOUR

The Titration of Mixtures

4. To date eighteen different metal cations (Mg, Ca, Sr, Zn, Cd, Pb, Cu, Ni, Co, Fe, Mn, Hg, Tl, La and the rare-earths, In, Bi, and Th) can be determined complexometrically by direct titration according to procedures of Type I and III. Five more cations (Al, Zr, Ag, Pd, and Na) and a few anions (SO_4, PO_4, CNS, CN, Cl, Br, and I) can be dealt with by back-titrations or indirect complexometric methods. All these titrations work perfectly when the solution contains the ion to be determined and that ion alone. But the titration of mixtures also presents a number of possibilities such as the determination of one particular constituent in the presence of others, or the simultaneous determination of several ions. The following fundamental considerations govern such procedures.

4.1. Ions Forming Complexes of Widely Differing Stability

When two metal cations differ considerably with respect to the stability of their complexes with EDTA, they will react with this complexing agent in discrete steps. As soon as the equivalent amount of EDTA has been bound to the metal which reacts first, there will be an abrupt decrease in its concentration before the other component of the mixture starts to form its EDTA complex. It is often possible to detect the first jump in pM by using the appropriate indicator.

Examples are provided by titrations of Fe(III) with Tiron or Variamine blue, and of Bi or Th with pyrocatechol violet in strongly acid solution ($pH = 2$ to 3); these titrations can be carried through without interference from any divalent metal cations present. Similarly it is possible to titrate Zn, Cd, Pb, and the lanthanons in the presence of the alkaline-earths, using Erio T as indicator, provided the titration is carried out at $pH = 7$ where the stabilities of the alkaline-earth complexes are all very small[23, 24, 25]. Dimethylnaphthidine (XIII) can be used for the determination of zinc in the presence of magnesium. A further example is the determination of calcium in the presence of magnesium in strongly alkaline solution using murexide (VI) as the indicator since this responds only to the calcium[211].

4.2. Use of Masking Reagents

It is often possible to 'mask' certain of the cations in a mixture so that they can no longer react with EDTA or with the indicator, and so are not included in the titre. Such masking can be effected by auxiliary complexing agents or by suitable precipitants. Masking can also be brought about in a number of cases by transforming the interfering ion into a different valency state.

The most effective masking agent is the cyanide ion[12, 199]; with its aid the cations of Co, Ni, Cu, Hg, Zn, Cd, Ag, and the platinum metals can be turned into stable cyanide complexes and then the alkaline-earths, the lanthanides, and Mn, Pb, or In can be titrated complexometrically in their presence. The two cations Zn^{+2} and Cd^{+2} can be liberated from their cyanide complexes by treatment with formaldehyde or chloral hydrate[116]. Both these aldehydes react with hydrogen cyanide to form cyanhydrins; the concentration of cyanide is reduced to such an extent that the cyanide complexes of zinc and cadmium are decomposed, though not those of Co, Ni, Cu, Hg, Ag, and Pt, whose stability constants are significantly greater. For example:

$$Cd(CN)_4^{-2} + 4H^+ + 4CH_2O \rightarrow 4HO\cdot CH_2\cdot CN + Cd^{+2} \quad (4.1)$$

These devices of masking and partial de-masking make it possible to carry out whole series of simultaneous determinations. If, for example, one cation from each of the groups: (i) Co, Ni, Cu, Hg; (ii) Zn, Cd; (iii) Mg, Ca, La, Mn, Pb, and In; is present in a mixture, cyanide can be used to mask the metals from the first two groups while the representative from the third is titrated. Then partial de-masking is effected and the zinc or cadmium is titrated. Finally the titre of EDTA is obtained in the absence of any other reagent and the total concentration of the three cations so obtained.

Other masking agents which operate through forming complexes are Tiron and triethanolamine[167]. Tiron can be used to mask Al^{+3} and Ti^{+4} in titrating the alkaline-earths or rare-earths when using Erio T as indicator. Al^{+3} and Ti^{+4} can also be masked by triethanolamine[189] as in the titration of nickel using murexide as indicator; it simultaneously suppresses interference due to traces of iron or manganese. Triethanolamine is also very suitable for reducing interference caused by Fe(III) and Mn in the titration of calcium in strongly alkaline solution using murexide[166, 167]. Unfortunately the interference caused by iron in titrations with Erio T as indicator in strongly ammoniacal solutions (in determinations of Mg, Ca, Zn, Cd, Mn, Pb, In) cannot be suppressed by triethanolamine.

Mercury can always be masked by iodide ions which are specific for this metal.

A masking agent frequently used is 2:3-mercapto-1-propanol (XIV), also termed BAL (British Anti-Lewisite)[181].

$$\mathrm{CH_2(SH)\cdot CH(SH)\cdot CH_2OH}$$

BAL (XIV)

It forms colourless, stable complexes with Hg, Cd, Zn, Sb, and Sn which dissolve smoothly in ammonia. Pb also gives almost colourless solutions and Bi yellow ones. On the other hand the complexes of Cu, Co, and Ni with BAL are dark-coloured and thus interfere with the titration end-point. BAL is especially valuable as a masking agent for Hg, Pb, and Bi in the titration of the alkaline-earths, and of Mn too. Of the metal-EDTA complexes, not only those of Mg, Ca, and Mn, but also that of Ni is not broken down by BAL; this introduces fresh possibilities for simultaneous titrations. One example is the titration of a mixture of Ni, Zn, and Mg. Addition of a known excess of EDTA and back-titration with $MgSO_4$ gives the total concentration of the three cations. BAL is then added to this titrated solution when the complex of zinc with BAL is formed and an equivalent amount of EDTA is set free; this is titrated with $MgSO_4$ to give the zinc content of the mixture. Finally KCN is added which forms a complex with the nickel and liberates an equivalent amount of EDTA which, as before, is determined by titration with $MgSO_4$. Instead of zinc, the mixture could have contained Cd, Hg, Pb, or Bi, and Ca in place of magnesium.

Among masking agents which operate by causing the precipitation of interfering substances, mention must be made of sulphides which are added, especially when determining the hardness of water[48], to suppress interference from small amounts of heavy metals that may be present, notably Fe or Cu. The same end is achieved using diethyldithiocarbamate in place of sulphide. On the other hand, the alkaline-earths, the rare-earths, and also Al and Ti can be masked by fluoride ions when Zn, Cd, Ni, or Co are to be titrated complexometrically[168].

Precipitation with diethyldithiocarbamate is used to effect an interesting determination of both Zn and Cd in a mixture of the two[166]. The total concentration of the two cations is first obtained by titration. When next diethyldithiocarbamate is added, the cadmium alone is precipitated and the equivalent of EDTA is set free; this can then be determined by a back-titration.

Masking by transforming a metal into a different valency state is especially easy to carry out in the case of copper. Reduction is brought about in acid solution by ascorbic acid or hydroxylamine. After making ammoniacal, Ni or Co can then be titrated using murexide as indicator without the copper, which is now present as Cu(I), interfering or being included in the titre. In a reducing medium, ferric iron can readily be changed into the ferrocyanide complex; while it otherwise reacts only slowly and incompletely with KCN, quick transformation to the ion, $Fe(CN)_6^{-4}$, is achieved after reduction with ascorbic acid.

4.3. Precipitation and Solvent Extraction

Instead of masking the ions which interfere and in this way making them harmless, the actual ion to be determined can also be precipitated or solvent extracted from the solution and then determined by a complexometric titration.

The following is a list of some of the precipitates which can be used for separations and in which, after being redissolved, the cations can easily be determined complexometrically: $Mg(NH_4)PO_4$[74, 75], $Mg(OH)_2$[151], oxalates of calcium[165] and the rare-earths, MnO_2, $Fe(OH)_3$, $Al(OH)_3$ $CoHg(CNS)_4$, $ZnHg(CNS)_4$, $CdHg(CNS)_4$, $Ni(Py)_2(CNS)_2$, Ni-dimethylglyoxime, CuCNS, Cu_2O, $PbSO_4$, $Bi(OH)_3$, PbClF, $CaMoO_4$[234], $CaWO_4$[232], $CaSO_3$[83], $CaSO_4$[18], $NaZn(UO_2)Ac_9$, 8-hydroxyquinolinates of various metals, etc. Pectin can be determined also by separating it as calcium pectinate and titrating the calcium in the precipitate[106]. $Zn_2P_2O_7$ or $Mn_2P_2O_7$ serve for the determination of pyrophosphate[273, 292].

It is interesting to note when considering such precipitations that an addition of EDTA or NITA—this time in the role of masking agent—introduces further possibilities of new types of separations[163, 164]. Thus thallium can be precipitated as iodide in the presence of other cations such as Pb; zinc as ZnS in the presence of Mn, Co, and Ni; bismuth as $Bi(OH)_3$ in the presence of many other metals[163, 165]; manganese as MnS in the presence of Ni, Zn, and Co; nickel as NiS in the presence of Co, Mn, and Zn; calcium as oxalate in the presence of Hg, Pb, Bi, Cu, Cd, As, Sb, Fe, Al, Cr, Ti, Be, U, Mo, W, Ce, Th, Ni, Co, Mn, Zn, and Mg[165];

phosphate as $Mg(NH_4)PO_4$ in the presence of Pb, Cu, Cd, Bi, Al, Fe, Ti, Bi, U, Sb, Sn, Ca, Sr, and Ba[109, 175]. Beryllium can be precipitated as $Be(NH_4)PO_4$ in the presence of many other metals[193], and sulphate as $BaSO_4$ in the presence of all the heavy metals if these are first masked with EDTA[177].

Zinc provides an example of the separation of the constituent to be determined by the process of solvent extraction. Separation from copper and lead is achieved by adding a large amount of thiocyanate and extracting with *iso*butyl methyl ketone; the extract is simply diluted and its zinc content determined without further ado by a complexometric titration[121, 122].

After the addition of cyanide, lead can be extracted with a solution of sodium diethyldithiocarbamate in chloroform and thus separated from Cu, Zn, Cd, Co and Ni. The extract is then shaken with a solution of $HgCl_2$ whereupon the lead in the organic phase is replaced by mercury. The lead is thus transferred once more to an aqueous phase and is titrated complexometrically after first masking the excess of mercury with iodide ions[123]. The specific extraction of Cu and of Bi can be accomplished in a similar way[43, 125].

4.4. Use of Ion-exchange Resins

Anions such as PO_4^{-3}, which may interfere in complexometric procedures, can be removed most speedily by using ion exchange resins. That the eluent occupies a large volume does not matter as a rule, for complexometric titrations work particularly well at high dilutions of 10^{-3} or 10^{-4} gram atoms/litre.

Ion exchange resins can also be used in other ways. To determine alkaline-earth metals in milk, the sample is allowed to pass down a cation exchange resin, the Mg^{+2} and Ca^{+2} are eluted with hydrochloric acid and titrated complexometrically[42]. The rare-earths can be separated on an ion exchange column by elution with EDTA[105, 246]. A column of anion exchange resin loaded with EDTA can be used to separate polyvalent cations from those of the alkali metals[191, 192]. Even a separation of Cs^+, Na^+, and Li^+ is possible[153].

CHAPTER FIVE

Solutions Used in Complexometric Titrations

5.1. Standard Solutions

5.1.1. *EDTA-solution.* The standard solution of this complexing agent is always prepared nowadays simply by dissolving its di-sodium salt ,Na_2H_2Y, in water. The di-hydrate of this salt is available commercially in a high degree of purity; it is also marketed under a variety of trade names such as Komplexon III* and "Versene". Ethylenediaminetetra-acetic acid (IV) itself is rather sparingly soluble in water and it is therefore impracticable to start out from this substance. Considered from the point of view of an analytical reagent, the di-sodium salt ought to contain as its sole impurity at most a trace of moisture. After drying at 80°C its composition agrees exactly with the formula $Na_2H_2C_{10}H_{12}O_8N_2$, $2H_2O$ (Formula weight 372·1) and it can be weighed out directly and treated as a primary standard[15, 223]. 37·21 g in 1,000 ml produces 0·1M–EDTA, 3·721 g in 1,000 ml produces 0·01M–EDTA, and 0·3721 g in 1,000 ml produces 0·001M–EDTA.

If the di-hydrate of the di-sodium salt is dried between 120° and 140°C there results the anhydrous salt of composition $Na_2H_2C_{10}H_{12}O_8N_2$ (Formula weight 336·1) which can serve equally well as a standard substance[46].

Care must be taken especially when making up dilute solutions of EDTA, to use water which contains absolutely no traces of polyvalent ions. Very often the ordinary distilled water used in the laboratory does not fulfill these requirements. To remove traces of copper or calcium it is sufficient to pass this water through a cation exchange resin in the sodium-ion form.

Solutions of the di-sodium salt, which have a pH of 4·8, keep extremely well and retain their titre unchanged for months provided they are kept in vessels of Pyrex (or similar borosilicate glass) which have been thoroughly steamed out before use. Polythene is also very suitable for storage vessels. In the course of time ordinary glass yields appreciable amounts of calcium to solutions of EDTA.

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* This is a registered trademark[233]. Cf. the footnote to the Translator's Preface.

If it is desired to standardise a solution of EDTA, the purest calcium carbonate[48], the purest zinc, or freshly distilled mercury can be used as primary standards. After solution the titration is carried out[16] by methods 6.5, 6.22.1, or 6.25.

5.1.2. *NITA-solution.* In the case of nitrilotriacetic acid (III) the starting material is the free acid which is available commercially (*e.g.* as Komplexon I) in an excellent degree of purity. The composition corresponds to $C_6H_9O_6N$ (Formula weight 191·1). It is unnecessary to dry this before use since solutions of NITA are never used as standard solutions, the results of titrations of Type IV being calculated from the volume of standard NaOH required. The acid is only slightly soluble in cold water. Neutral solutions of the di-sodium salt are prepared as follows: 0·1M–NITA. Commercial nitrilotriacetic acid (19·11 g) and solid NaOH (7·5 g) are dissolved by warming in about 200 ml water. After cooling, a few drops of methyl red are added and the solution is titrated with approximately 0·1N–NaOH until the last trace of reddish shade has gone. Then dilute to 1000 ml with water. The solution has a pH of about 6·0 and contains the di-sodium salt, Na_2HX.

5.1.3. *Standard Metal Solutions.* Standard solutions of magnesium sulphate or zinc sulphate are required for back-titrations. These are prepared by weighing out approximately the desired amount of $MgSO_4$, $6H_2O$ or $ZnSO_4$, $7H_2O$ respectively and standardising with a solution of EDTA of known concentration. A standard solution of $MnSO_4$ can also be used[282].

5.1.4. *Magnesium and Zinc Complexonate.* 0·1M–MgY and 0·1M–ZnY. The magnesium complex of EDTA is needed in the substitution titrations (Type III). For this purpose the sodium salt, Na_2MgY, $4H_2O$, is available commercially and can be used directly, provided its purity is adequate. However, one ought never to neglect testing whether the sample does in fact contain Mg and EDTA in the ratio 1:1. A solution of the salt ought to have a pH between 8 and 9; after adding some NH_3—NH_4^+ buffer of pH = 10, a few drops of Erio T should produce a dirty violet colour which should turn to blue with a single drop of 0·01M–EDTA, and to red with a single drop of 0·01M–$MgSO_4$. The sodium salt of the zinc-EDTA complex also crystallises with four molecules of water, Na_2ZnY, $4H_2O$; it is dealt with in the same way.

The magnesium- and zinc-complexonates can readily be prepared in the following way. Equivalent amounts of solutions of EDTA and magnesium sulphate (or zinc sulphate) are mixed and neutralised with NaOH to a pH between 8 and 9 (phenolphthalein just reddened). Then the test with Erio T is carried out and on its result the necessary deficiency of metal or EDTA made good. Finally the solution is diluted to a known concentration, *e.g.* 0·1M or 0·01M. These complexonate solutions do not need standardising.

5.1.5. *Standard NaOH.* For titrations of Type IV, a supply of 0·1N–NaOH is required; this is conveniently standardised against the solution of EDTA[223]. To this end, rather more than the equivalent amount of neutral zinc sulphate is added to a known volume of standard EDTA solution; for each mole of EDTA two gram ions of hydrogen are liberated and the resulting acidity is neutralised by the alkali which is to be standardised, using methyl red as the indicator. 40 ml of 0·1M–NaOH are required for every 20 ml of 0·1M–EDTA (cf. reaction 2.4).

5.2. Indicators

5.2.1. *Eriochrome Black T (V).* Dissolve 0·2 g of the dyestuff in 15 ml triethanolamine and 5 ml absolute alcohol. Such solutions keep for at least a month[49].

5.2.2. *Murexide (VI).* About 0·5 g of the powdered dyestuff is suspended in water, thoroughly shaken, and the undissolved portion allowed to settle. The saturated supernatant liquid is used for titrations. Every day the old supernatant liquid is removed by decantation and the residue treated with water as before to provide a fresh solution of the indicator.

5.2.3. *Metalphthalein (VII).* Add a few drops of concentrated ammonia to a mixture of 0·18 g cresolphthalein-bis (methyliminodiacetic acid) (VII) and 0·02 g naphthol green (Schultz-Lehmann, No. 5), and dilute to 100 ml. The solution keeps for some weeks.

5.2.4. *Tiron.* Use a 2% solution of the di-sodium salt of pyrocatechol disulphonic acid. The colourless solution keeps for a long time.

5.2.5. *Pyrocatechol Violet (VIII).* Dissolve 0·1 g of the commercial indicator in 100 ml water. The solution keeps for a few months.

5.2.6. *Methyl Red.* 0·1 g dissolved in 100 ml of ethanol.

5.2.7. *Methyl Red—Bromocresol Green.* 0·1 g methyl red and 0·15 g bromocresol green are ground up together and dissolved in 100 ml of ethanol.

5.3. Buffers

The following buffering materials are recommended for the various pH ranges:

pH = 1. Stock N-HCl can be used as a buffer solution.

pH = 2–4. p-Chloroaniline and its hydrochloride. The solid base is used to make up solutions of higher acidity as required. Glycine is also effective in this buffer region.

pH = 4–6·5. Acetate-acetic acid. Supplies of N-acetic acid and N-sodium acetate are kept ready, and mixed as required.

pH = 6·5–8. Triethanolamine and its hydrochloride. Solutions of M–$N(C_2H_4OH)_3$ and M–HCl are kept in stock and mixed as required. In using this buffer mixture it is essential to take account of the fact that triethanolamine is a chelating agent; as such it can form complexes of considerable stability with many metal cations, a result which is undesirable from the point of view of most titration procedures as it decreases the jump in pM at the end-point. The concentration of free triethanolamine must therefore be kept as low as possible. Malic acid and veronal suffer from the same disadvantages for this pH range. Phosphate buffers are completely impracticable in view of the precipitation of metal phosphates. Imidazole, whose 'onium salt has a pK value of almost exactly 7, and which is not favourably constituted for the formation of chelate complexes, would be an ideal substance for a buffer covering pH 6–8. However the high cost of imidazole puts it out of the picture.

Buffering in the neighbourhood of pH = 7 can be effected very well with NH_3–NH_4^+. Naturally the buffer capacity is only small, *e.g.* $[NH_4^+] \sim 0{\cdot}1$ and $[NH_3] \sim 10^{-3}$. The pH can readily be adjusted by testing drops with indicator paper; if it falls too low a drop of ammonia can be added. In this way almost ideal conditions are provided, for the extent of complex formation by the constituents of the buffer is extraordinarily small.

pH 8–11. Ammonia-ammonium salt. Solutions of M–NH_4OH and M–NH_4Cl are kept ready and mixed as required. Glycine and borate buffers cannot be recommended since the glycine- and borate-complexes are as a rule significantly stabler than the ammine complexes. Besides, borate ions give precipitates with several metals.

pH = 10. A buffer of pH about 10 is often wanted. It is prepared by adding 570 ml concentrated ammonia (density 0·90) to 70 g ammonium chloride and making up to 1000 ml.

The purest chemicals must be used for this buffer. Commercial '0·880' ammonia often contains small amounts of alkaline earths and it is better to prepare the ammonia solution by using gas from a cylinder.

pH = 12–13. N–NaOH solution is satisfactory in this buffer region.

5.4. Masking and De-masking Agents. Oxidants and Reductants

Masking agents. KCN, Na_2S, NaF, triethanolamine, Tiron, sodium diethyldithiocarbamate, hydroxylamine, dimercaptopropanol (BAL, XIV)[181].

De-masking agents. 30% formaldehyde, chloral hydrate.

Reducing agents. Ascorbic acid, hydroxylamine sulphate.

Oxidising agents. Hydrogen peroxide, potassium persulphate.

All these reagents ought to be free from metals, more especially calcium. Tests from this point of view are carried out particularly on KCN, Na_2S, and the formalin solution by adding a buffer of pH = 10 and then Erio T which should give a clear blue colour.

CHAPTER SIX

Details of Procedures

In the following detailed procedures the various elements are dealt with in the order in which they appear in the 'long-period' form of the periodic table, *i.e.* in the following order: alkaline earth metals; Sc, Y, La; Ti, Zr, Th; Mn, Fe, Co, Ni, and Cu; Zn, Cd, Hg; Al, Ga, In, and Tl; Pb and Bi. Indirect methods are collected at the end.

6.1. Alkalimetric Titrations of Metals with EDTA (Type IV, section 2.2.4.1)[199, 209, 223]

Applications. Rapid determination of divalent cations, *e.g.* Mn, Co, Ni, Cu, Zn, Cd, Hg, and Pb, with NaOH. All the rare-earths can be similarly titrated. If several metals are present the total concentration is obtained. The method is to be recommended particularly as a preliminary titration for ensuring the smallest possible excess of EDTA for a procedure involving a back-titration.

REAGENTS. Standard 0·1N NaOH as titrant; methyl red-bromocresol green indicator; 0·1M–EDTA; M–NH_4Cl.

PROCEDURE. The solution of metal cation to be determined, which must not contain a weak acid or a salt of a weak acid, is treated with ammonium chloride (10 ml for each 100 ml solution), and after adding indicator is brought to pH $\sim$ 5 with NaOH (indicator turns grey). This neutralisation of excess acid present must be carried out with great care. In the next stage, the addition of EDTA, it must be remembered that the jump of pH at the end-point is better defined the smaller the excess of EDTA employed. (cf. Fig. 16). The solutions of EDTA and NaOH are therefore placed in two adjacent burettes. First a few ml of EDTA are added and neutralisation is at once effected with the standard alkali. Then a further small amount of EDTA is added and the neutralisation carried out again. These operations are repeated until finally the addition of EDTA no longer causes the pH to sink below pH = 5.

CALCULATION. The result is calculated from the volume of standard alkali required. Each ml of 0·1N–NaOH corresponds to $0{\cdot}5 \times 10^{-4}$ gram atoms of metal, *i.e.* to 2·746 mg Mn; 2·947 mg

Co; 2·935 mg Ni; 3·177 mg Cu; 3·269 mg Zn; 5·620 mg Cd; 10·03 mg Hg; 10·36 mg Pb.

Remarks. This procedure can also be carried out on a suspension of $PbSO_4$ which slowly goes into solution during the titration. The presence of the coloured cations Co, Cu, Ni, gives rise to some trouble in seeing the end-point. The trivalent cations Fe^{+3}, Cr^{+3}, Al^{+3}, etc., cannot be titrated by this procedure since the preliminary neutralisation cannot be carried out because of the hydrolysis of the aquo-cations.

6.2. Alkalimetric Titrations of Metals with NITA (Type IV, section 2.2.4.2)[199, 209, 223]

APPLICATIONS. The procedure is applicable generally to the determination of Mn, Co, Ni, Cu, Zn, Cd, Hg, Pb, and the rare-earths. If several metals are present the total concentration is obtained.

REAGENTS. Standard 0·1N–NaOH as titrant; methyl red; 0·1M—NITA (previously neutralised); M–NH_4Cl.

PROCEDURE. To the solution of the metal to be determined, which must contain no weak acid or a salt of a weak acid, add a few drops of methyl red and 10 ml of ammonium chloride for each 100 ml of solution. If there is any excess of acid, neutralise it carefully with NaOH. Now add a few ml of NITA solution and neutralise the resulting acidity with the standard NaOH. Alternately add NITA and neutralise again until finally the addition of NITA produces no further drop in pH.

CALCULATION. The result is calculated from the volume of standard alkali used. Each ml of 0·1N—NaOH corresponds to 10^{-4} gram atoms of metal, *i.e.* to 5·492 mg Mn; 5·894 mg Co; 5·869 mg Ni; 6·354 mg Cu; 6·538 mg Zn; 11·241 mg Cd; 20·061 mg Hg; 20·721 mg Pb.

REMARKS. Precipitated lead sulphate can also be titrated as a suspension. More indicator must be used if coloured ions, *e.g.* Cu, Ni, Co, are present. Apart from the rare-earths, trivalent metal cations cannot be titrated since their solutions can not be preneutralised.

6.3. Iodometric Finish to Procedure 6.2.

APPLICATIONS. This variation works satisfactorily with Co, Ni, Zn, and Pb. Lead must first be precipitated as sulphate and then titrated in suspension.

REAGENTS. Standard 0·1M–Thiosulphate as titrant; neutral

0·1M–NITA; iodate solution (21·5 g KIO_3 per litre); iodide solution (83 g KI per litre); starch solution; M–NH_4Cl.

PROCEDURE. The weakly acid test solution is treated with 10 ml ammonium chloride for each 100 ml, and with some iodide and iodate. Liberated iodine is decolorised by adding thiosulphate. Now for each milliatom of metal to be titrated at least 10 ml NITA is added together with 3 ml iodate and 3 ml iodide solution. Titration is carried out with standard thiosulphate, starch solution being added just before the end-point. If it is desired to use starch in the preliminary titration (*i.e.* the neutralising of excess acid), the actual titration should be carried out with a fresh portion.

CALCULATION. Each ml 0·1M–thiosulphate corresponds to 10^{-4} gram atoms of metal, *i.e.* to 5·894 mg Co; 5·869 mg Ni; 6·538 mg Zn; 20·721 mg Pb.

REMARKS. Cu^{+2} and Hg^{+2} interfere; so do those trivalent cations which effect the liberation of iodine by their own hydrolysis.

6.4. Direct Titration of Magnesium with Erio T[12, 133, 199, 227]

APPLICATIONS. Determination of magnesium after removing other alkaline-earth metals. Any Ca, Sr, and Ba present are estimated simultaneously in the titration; furthermore Sr and Ba cause the end-point to be drawn out. When the heavier alkaline earths are present, however, they can be separated by precipitation with $(NH_4)_2CO_3$ and the magnesium determined in the filtrate by direct titration. Mn, Cr, Fe, Al, Pb, Bi, Sb, Ti, Zr, Th, rare-earths, Pb, Ta, Ga, and In should be removed, *e.g.* by precipitating their hydroxides with acetate or NH_3–NH_4^+. Any iron left behind as a colloid in solution interferes badly and can only be rendered harmless by the addition of Na_2S. BAL can be used to mask Pb, Cu, Cd, Hg, and Bi. Metals which form ammines, *e.g.* Co, Ni, Cu, Zn, Hg, and the platinum metals, can be masked with KCN. Oxalate produces a drawn out end-point since magnesium forms an oxalato-complex. The determination of magnesium can still be carried out if small amounts of phosphate are present if the titration is performed rapidly[266]. If calcium is present it can be precipitated as $CaWO_4$ or

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; buffer of pH = 10.

PROCEDURE. The sample solution should contain magnesium in a concentration not greater than 10^{-2}. Acidic solutions are first neutralised with NaOH. To every 100 ml solution add 2 ml buffer and 2–4 drops of Erio T and titrate to the colour change from red to blue. The last trace of a reddish shade should disappear with the last drops of titrant. Since complex formation does not take place instantaneously, the titration must be carried out slowly near the end-point.

CALCULATION. Every ml 0·01M–EDTA corresponds to 10^{-5} gram atoms of magnesium, *i.e.* to 0·2432 mg.

REMARKS. From Fig. 30, which is obtained by combining Figs. 4 and 19, it is clear that the pH should be kept pretty close to 10 throughout the titration. Both too low and too high a pH will worsen the end-point. On this account the acidity in sample solutions should be neutralised with NaOH and not NH_4OH, so as not to introduce additional ammonium ion into the solution.

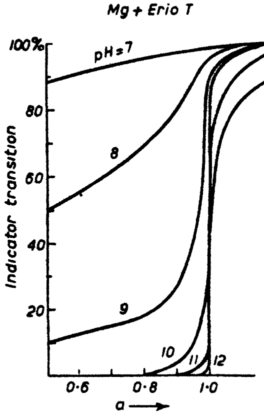


FIG. 30

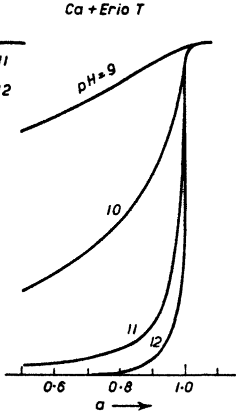


FIG. 31

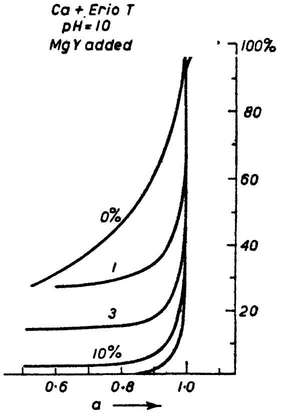


FIG. 32

FIG. 30. Colour transition of Erio T during the titration of Mg at various pH values

FIG. 31. Colour transition of Erio T during the titration of Ca at various pH values

FIG. 32. Colour transition of Erio T during the titration of mixtures of Mg and Ca at pH = 10. The Mg content of the solution is varied and shown as a percentage of the amount of Ca present

With the right choice of conditions the end-point is so sharp that the titration can be carried out even with 0·001M–EDTA.

6.5. Substitution Titration for Calcium Using Erio T

APPLICATIONS. Determination of calcium when magnesium is absent or has been removed. Sr and Ba are included in the titre if present and they also cause a rather drawn out end-point. Mn, Cr, Fe, Al, Pb, Bi, Sb, Ti, Zr, Th, rare-earth metals, Bi, Nb, Ta, Ga, and In must be removed. Iron interferes if it remains even in the smallest amount in colloidal solution and can only be rendered harmless with Na_2S. Co, Ni, Cu, Zn, Cd, Hg, and the platinum metals can be masked with KCN. Sb, Pb, and Bi can be masked with BAL[181].

REAGENTS. Standard solution of 0·01M–EDTA as titrant; Erio T; buffer of pH = 10; 0·1M–MgY.

PROCEDURE. The concentration of calcium in the test solution should not exceed 10^{-2}. If it is acid, it must be neutralised with NaOH. To every 100 ml of test solution add 2 ml buffer, 1 ml of 0·1M–MgY, and 2–4 drops of Erio T; titrate until the colour changes from red to blue. The last trace of reddish hue should disappear at the end-point. Titrate slowly near the end-point.

CALCULATION. Every ml. 0·01M–EDTA corresponds to 10^{-5} gram atom of Ca, *i.e.* 0·4008 mg.

REMARKS. Fig. 31, which is a combination of Figs. 5 and 20 shows how the colour of Erio T changes when calcium is titrated in the absence of magnesium. Even at pH = 11 there is seen to be no sharp end-point and furthermore the transition is not to a pure blue, for we are already in the pH region where Erio T is acting as an acid-base indicator with HD^{-2} (blue) → D^{-3} (brown).

Fig. 32 demonstrates the effect of adding magnesium (as its EDTA complex). Since the calcium complex, CaY^{-2}, is stabler than the magnesium complex, the one metal replaces the other so that we are really dealing with a simultaneous titration of Ca + Mg, details of which have already been given in Fig. 11. Fig. 32 was constructed using values of pMg from Fig. 11 in conjunction with the colour transition curve of Fig. 19. It shows how even the addition of so little as 1% Mg considerably improves the end-point. The maximum attainable effect is practically reached with a 10% excess, and any further addition of MgY^{-2} will merely increase the ionic strength unnecessarily and make the jump in pMg somewhat smaller again.

With the correct choice of conditions the colour change is so sharp that it is possible to carry out a micro-titration with 0·001M–EDTA.

6.6. Determination of Calcium and Magnesium together with Erio T; the Hardness of Water [8, 11, 12, 18, 22, 27, 46, 85, 126, 140, 141, 220]

APPLICATIONS. Determination of the content of alkaline earths in water from any source. This new method works very well for water from Permutite softeners and also for sea-water[233]. It can also be used for determinations of alkaline earths in rocks[7], soils[41], cements[113], slags[87], salts[231], glasses[44, 154], biological materials[29, 50, 104, 107, 112, 144, 249, 6, 42], and pharmaceutical products. Sr and Ba, if present, are included in the titre; but they also cause the end-point to be drawn out. Since the titration is carried out in alkaline solution, many metals do not interfere or are precipitated on the addition of the buffer, *e.g.* Mn, Fe, Al, Cr, Pb, Bi, Sb, Ti, Zr, Th, rare-earth metals, Be, Nb, Ta, Ga, and In. Of these, iron can remain in colloidal solution and then interferes even when present in the merest trace. Its interference can be suppressed by adding Na_2S. Sb, Bi, and Pb can be masked with BAL[181]. The metals Co, Ni, Cu, Zn, Cd, Hg, and the platinum metals, which are not precipitated in ammoniacal solution but form ammine complexes, can be masked with KCN. Phosphate must be removed[27, 45] by means *e.g.* of an ion exchange resin. Alternatively the titration must be carried out rapidly[266].

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; buffer of $pH = 10$; and if required 0·1M–MgY, and masking agents for iron and copper.

PROCEDURE. To 100 ml of the sample of water add 2 ml of buffer, masking agents as required, 2–4 drops of Erio T, and titrate at once to the colour change from red to blue. The last trace of red vanishes at the end-point.

If the water undergoing examination contains no magnesium, some magnesium complexonate must be added, *i.e.* procedure 6.5 must be used.

CALCULATION. Every ml 0·01M–EDTA corresponds to 10^{-5} gram atom of metal, *i.e.* to 0·4008 mg Ca, or 0·561 mg CaO, or 1·001 mg $CaCO_3$. In terms of degrees of hardness, the consumption of 1 ml 0·01M–EDTA for each 100 ml sample of water corresponds to 0·561 German degrees of hardness, 1·001 French degrees of hardness, 1·43 grains $CaCO_3$ per gallon, or 10 parts $CaCO_3$ per million.

REMARKS. Somewhat sharper end-points are obtained if the water sample is first acidified with HCl, and boiled for about 1 minute to drive off CO_2. After cooling, neutralise with NaOH, and then add buffer, and indicator, and carry out the titration.

The effect of the magnesium is dealt with in the remarks appended to procedure 6.5 given above. Here a very full discussion is given of the reasons why the deliberate addition of this element in the form of its complexonate, even in quite small amounts, is so effective in improving the sharpness of the end-point.

6.7. Substitution Titration of Strontium and Barium with Erio T[108, 229]

6.7.1. *Procedure Using Magnesium Complexonate.*

APPLICATIONS. Determination of Sr or Ba, when Ca and Mg are absent. As in procedures 6.4, 6.5, and 6.6 heavy metals must be absent or have been masked by KCN.

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; buffer of pH = 10; 0·1M–MgY.

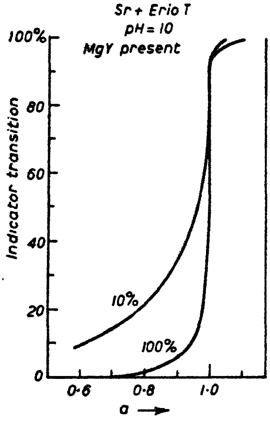


FIG. 33

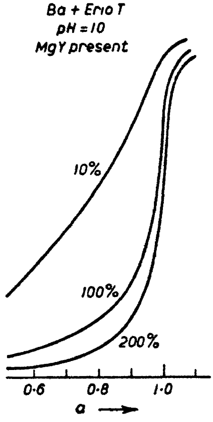


FIG. 34

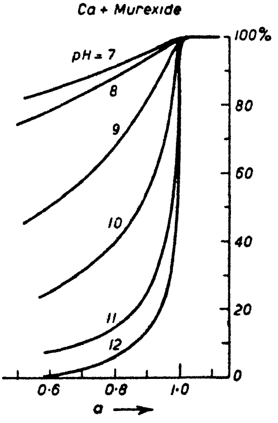


FIG. 35

FIG. 33. Colour transition of Erio T during the titration of mixtures of Sr and Mg at pH = 10. The Mg content of the solution is varied and shown as a percentage of the amount of Sr present

FIG. 34. Colour transition of Erio T during the titration of mixtures of Ba and Mg at pH = 10. The Mg content of the solution is varied and shown as a percentage of the amount of Ba present

FIG. 35. Colour transition of murexide during the titration of Ca at various pH values

PROCEDURE. The test solution is first neutralised with NaOH. To each 100 ml add 10 ml 0·1M–MgY, 2 ml buffer, and 2–4 drops of Erio T. Then titrate with EDTA until the colour changes from red to blue.

CALCULATION. Each ml of 0·01M–EDTA corresponds to 10^{-5} gram atoms of metal, *i.e.* 0·8763 mg Sr, or 1·3736 mg Ba.

REMARKS. The change of colour is less sharp with Sr than in the corresponding titration of Ca (6.5) and still less so with Ba. This is due to the relative stability of the various complexes. With barium, the stability constant of BaY^{-2} is only $10^{7·8}$ as compared with the value $10^{8\cdot7}$ for MgY^{-2}, the complex formed by the cation to which the indicator is sensitive. Thus, on adding the complexing agent, the magnesium disappears from the solution before the barium, and the end-point appears too soon. This point is brought out in Figs. 33 and 34 which were obtained by combining values of pMg from Figs. 12 and 13 with the colour transition curve of the indicator given in Fig. 19. They show how the change in colour begins well before the true end-point, and is complete at the point of equivalence. The situation is somewhat improved by taking a large excess of magnesium complexonate.

6.7.2. *Procedure Using Zinc Complexonate.*

APPLICATIONS. As for procedure 6.7.1. This procedure is specially recommended for the back-titration of barium after its precipitation as sulphate, and also for the determination of sulphur[240].

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; concentrated NH_4OH; 0·1M–ZnY; approximately M–NH_4Cl.

PROCEDURE. 100 ml of the test solution, which must not contain more than 5×10^{-4} gram atoms of barium or strontium is neutralised, if necessary, with sodium hydroxide and then treated with 10 ml of standard zinc complexonate and 1 ml of ammonium chloride. Sufficient ammonia is then added to make the mixture about 0·5 M with respect to this base (3–4 ml 25% NH_4OH per 100 ml sample). After introducing the indicator the titration is carried out until the colour changes from red to blue.

CALCULATION. As in procedure 6.7.1.

REMARKS. As explained in the theoretical section, sufficient ammonia must be added to bring the magnitude of the coefficient β_A for the zinc to about 10^8. At the equivalence-point there is then a really well-defined jump in pZn as shown in Fig. 15. At pH = 11 this is better defined than at pH = 10, but the higher pH is necessary in any case to bring the jump in pZn into line with the transition interval for the indicator as shown in Fig. 21. Erio T changes colour too soon at pH = 10 as shown in the broken curves of Fig. 36. However, at pH = 11 the indicator transition shown in Fig. 21 coincides exactly with the steep rise in pZn shown in Fig. 15. A combination of Figs. 15 and 21 leads to the curves for pH = 11 shown as solid lines in Fig. 36.

To reach a pH value of 11 with the ammonia buffer, the concentration ratio $[NH_4^+]/[NH_3]$ need only amount to 0·02. In 0·1M–NH_3, the most favourable ammonia concentration, the concentration of ammonium salt should therefore be about 0.01 mol/l.

6.7.3. *Back-titration of Barium.* Instead of a substitution titration, it is often preferable to carry out a back-titration using 0·01M-zinc sulphate. This is particularly appropriate for the determination of barium in a precipitate of $BaSO_4$. The precipitate is suspended in an accurately measured volume of 0·1M–EDTA (about a two-fold excess) and 4 ml of concentrated ammonia (25%) added. After this addition of base the precipitate slowly goes into solution at the boiling point. Fresh ammonia must be added to replace any which evaporates. Then 1 ml of 1M–NH_4Cl is added, together with indicator, and after diluting to about 100 ml the excess of EDTA is back-titrated with a standard zinc solution until the colour changes from blue to red. At the equivalent point $BaSO_4$ starts to separate out again for its solubility product has been exceeded. While taking the $BaSO_4$ into solution there is a possibility of extracting alkaline earth ions (which would be included in the titre) from the vessel used,

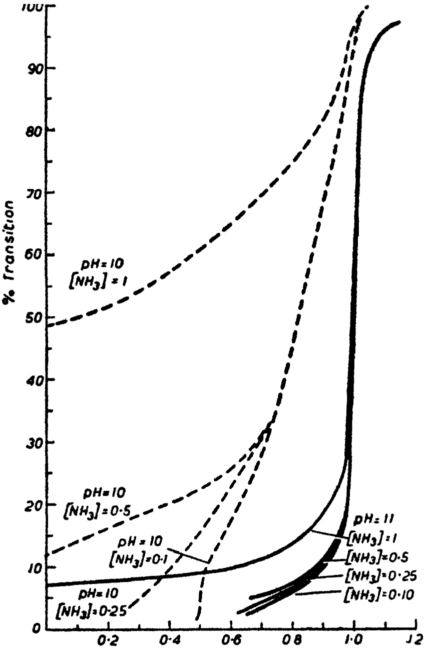


FIG. 36. Colour transitions of Erio T during the titration of equivalent amounts of Ba and Zn at pH = 10 (broken curves) and at pH = 11 (solid curves), and for various concentrations of ammonia

should this be made of glass. It is of advantage to work in beakers of silica or boro-silicate glass.

6.8. Direct Titration of Calcium with Murexide[6, 32, 199, 223, 211]

APPLICATIONS. Determination of calcium in water, biological fluids, plant materials[38, 88], limestone[7, 40], cement, minerals, and soil samples[38], slags, and pharmaceutical products[89]. Heavy metals must be absent or separated as *e.g.* hydroxides. Small quantities of Fe, Mn, and Ti can be masked with triethanolamine[167], and Co, Ni, Cu, Zn, Cd, Hg, and Pt (from platinum crucibles) with KCN. Sb, Bi, Cu, Zn, Cd, Hg, and Pb can be masked with BAL[181]. The titration can be carried out in the presence of magnesium (see remarks) and barium. Strontium is included in the titre and causes a drawn out end-point. By titrating rapidly, the determination can be carried through even when phosphate ions are present in small amounts[266]. If large amounts of phosphate are present the end-point comes too soon and is drawn out. Phosphate ions should therefore be removed with an anion exchange resin.

REAGENTS. Standard 0·01M–EDTA as titrant; murexide; N–NaOH; 0·01M–$CaCl_2$ if required.

PROCEDURE. To every 100 ml of the neutral solution to be analysed (acid solutions must be neutralised with NaOH), and containing not more than 5 mg Ca, add 10 ml N–NaOH and, where necessary, masking agent. Then add a few drops of indicator and titrate at once to a colour change from red to violet. The titration must be carried out straight away on account of the danger of precipitation of $CaCO_3$.

CALCULATION. Every ml of 0·01M–EDTA corresponds to 10^{-5} gram atom, *i.e.* to 0·4008 mg Ca.

REMARKS. The change in colour at the end-point is displayed in Fig. 35 which is a combination of the values of pCa given in Fig. 5 with the colour transition graph for murexide given in Fig. 23. It is obvious that the titration must be carried out above pH = 12. Even here the indicator changes colour at too low a value of pCa; this causes the peculiar shape of the transition curve shown in Fig. 35 with its abrupt change of direction at $a = 1$ mol. EDTA per mol. Ca, and 100% transformation of colour. Although this occurs exactly at the equivalence point, it is hard to detect visually since the titration has to be carried to the point where the last trace of red has gone. It is, however, possible to increase the accuracy of the method very considerably by carrying out a photometric titration, *i.e.* by measuring the absorbancy after successive additions of EDTA, best at 480 or 590 mμ (cf. the absorption spectrum in Fig. 22 of CaH_2D^-, the calcium-indicator complex, and that of H_2D^{-3} due to murexide in alkaline solution).

The broken curves for pCa in Fig. 14 are of importance when considering the conditions for titrating calcium in the presence of magnesium. $Mg(OH)_2$ is so sparingly soluble in the strongly alkaline solutions of pH = 13 that the titration of calcium left in solution furnishes just as good a jump in pCa as if magnesium were absent (cf. Fig. 14, broken curve II). If, in fact, the solution is first made alkaline, and allowed to stand for 1–2 minutes until the hydroxide precipitate has formed, addition of indicator and titration with EDTA leads to an easily detectable end-point. However, the results for calcium come a few per cent low since some is carried down on the precipitate. After the first end-point has been reached, a part of this calcium returns into solution; so that on standing, the murexide goes red again, and more titrant can be added.

An addition of sucrose is said to improve the end-point[17].

If only a very little magnesium is present, the $Mg(OH)_2$ does not separate out straight away and there is time to titrate the supersaturated solution. The broken curve I of Fig. 14 corresponds to such a titration and it is clear that when all the calcium has been complexed by EDTA (at $a = 0{\cdot}5$) a small jump in pCa takes place. Nevertheless this is shown up quite satisfactorily with murexide so that correct figures for calcium are obtained, and the precision is only slightly less than in the complete absence of magnesium. This is the position in determining the calcium hardness of natural waters.

However, in order to obtain correct results in the presence of a lot of magnesium (*e.g.* in the analysis of magnesite), the procedure is to complex the calcium first of all with a small excess of EDTA and then to make alkaline, when pure magnesium hydroxide is precipitated without any inclusion of calcium; the excess of EDTA is then back-titrated. The actual procedure will be on the following lines[78]:

500 Ml of the solution of magnesite, which must not contain more than about 20–40 mg of calcium, is placed in a 1000 ml volumetric flask. EDTA is added in an amount slightly in excess of the calcium content (determined roughly in a preliminary titration), together with 2 ml triethanolamine (to mask iron and manganese). The solution is neutralised and then made strongly alkaline by the

addition of 100 ml N–NaOH. After making up to the mark, and mixing, the flask and contents are allowed to stand for 30 minutes. 200 ml of the clear liquid standing over the precipitated magnesium hydroxide is withdrawn with a pipette, and after the addition of indicator the small excess of EDTA is back-titrated with 0·01M–$CaCl_2$. The difference between the volume of EDTA originally taken and the titre of $CaCl_2$ required is used in the calculation. Addition of sucrose ought to improve the titration of calcium in the presence of magnesium.

Many authors state that the colour change of murexide is seen more easily when naphthol green is also present in the ratio 2:5 of the two dyestuffs[127].

There is also the possibility of precipitating magnesium hydroxide in the presence of much calcium by adding mannitol. Ca can be titrated in the filtrate, and the precipitated $Mg(OH)_2$ can be determined[151] by procedure 6.4.

Conversely the calcium can be precipitated as $CaSO_3$. Magnesium can be determined in the filtrate after boiling off SO_2, and calcium titrated after dissolving the precipitate in acid[83].

6.9. Direct Titration of Calcium with Metalphthalein (VII).

APPLICATIONS. As in procedure 6.5; but in contrast to this there is the advantage that the phthalein indicator (VII) is less sensitive to traces of heavy metal impurities, particularly iron and copper.

REAGENTS. Standard solution of 0·01M–EDTA as titrant; metalphthalein-naphthol green; M–NH_4OH; M–NH_4Cl.

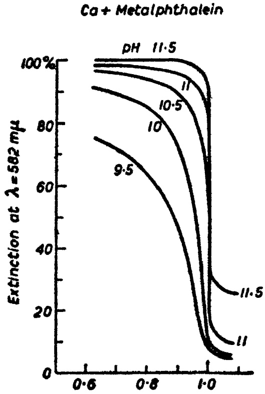
PROCEDURE. The solution to be titrated should contain between 10^{-3} and 10^{-4} gram atoms Ca per litre. Acidic samples should first be neutralised with NaOH. Then add for each 100 ml of sample 0·3 ml indicator, 5 ml NH_4OH, and if necessary (see later) a few drops of NH_4Cl. Titrate with EDTA until the red colour suddenly goes pale; the fully titrated solution is grey.

CALCULATION. Every ml of 0·01M–EDTA corresponds to 10^{-5} gram atoms of Ca, *i.e.* to 0·4008 mg.

REMARKS. The change in optical absorption during this titration is shown in Fig. 37 which was obtained by combining Figs. 5 and 28. It can be seen that it is advantageous to work at pH = 11 or a little below. If the pH is lowered to 10, the change in intensity is drawn out and no longer sudden; if the pH is above 11, the intensity of the red colour at the end-point is quite appreciable. At pH = 10·5–11, the absorbancy at the end-point is only about

10–13% of what it was at the beginning. This proportion of red is made invisible by the admixed naphthol green.

In order to reach pH = 11 with an ammonia buffer, it is essential that only a small quantity of ammonium ions should be present. As a rule the hydrogen ions resulting from complex formation according to equation (2.4) suffice to turn enough NH_3 to NH_4^+. Should that not prove to be the case, as shown by an intense red colour persisting at the end-point, a few drops of ammonium chloride solution are added.



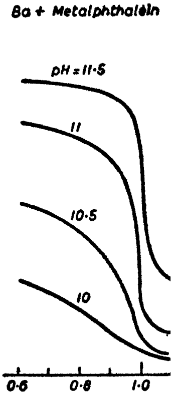


FIG. 37 FIG. 38

FIG. 37. Colour transition of metalphthalein (VII) during the titration of Ca at different pH values

FIG. 38. Colour transition of metalphthalein (VII) during the titration of Ba at different pH values

Particularly good results are obtained when the end-point is obtained photometrically[114].

6.10. Direct Titration of Barium (or Strontium) with Metalphthalein[4]

APPLICATIONS. Determination of barium (or strontium) in the absence of other alkaline earth metals, *e.g.* after precipitation as sulphate (cf. procedure 6.34). Most heavy metals are precipitated in the strongly alkaline solution; those which form ammine complexes are masked with KCN.

REAGENTS. Standard solution of 0·01M–EDTA as titrant; standard solution of 0·01M–$BaCl_2$ for back-titration; metalphthalein-naphthol green; concentrated ammonia; M–NH_4Cl if required; ethanol.

PROCEDURE. To every 100 ml of neutral test solution (acidic samples are first neutralised with NaOH), which must have a metal concentration between 5 × 10^{-3} and 5 × 10^{-4} gram atoms per litre, add 0·3 ml indicator and 5–10 ml ammonia. In view of the danger of $BaCO_3$ precipitating, the titration is started off at once, the end-point being identified by the sudden weakening of the red colour. Should the solution retain a fairly strong red colour after overshooting the end-point, lower the pH by adding some ammonium chloride. After a small excess of EDTA has been added, introduce sufficient ethyl alcohol to make a 50% mixture, and back-titrate with standard barium solution. The addition of the alcohol causes a change in colour from grey to green (due to the naphthol green) and at the end of the back-titration there is a sharp return to red.

CALCULATION. Every ml 0·01M–EDTA corresponds to 1·3736 mg Ba, or 0·87639 mg Sr.

REMARKS. Changes in the colour intensity of aqueous solutions of metalphthalein during the forward titration are shown in Fig. 38 which is derived from Figs. 6 and 28. It follows that in this titration the pH value of 11 must be established really precisely. Even at pH = 10·5 the change in colour is too drawn out, while at pH = 11·5 some 30% of the original red colour remains at the end-point. The situation at the end-point is improved considerably by adding alcohol; but this must only be introduced for the back-titration as otherwise $BaCO_3$ generally separates straight away.

6.11. Direct Titration of Rare Earths with Erio T

APPLICATIONS. Direct determination of the light rare-earths with Erio T. (The heavy earths of atomic number over 64 cannot be titrated in this way[269]. Determination of total lanthanons after the separation of interfering metals, *e.g.* after a preliminary precipitation of rare earth oxalates. Ti, Al, Fe, Bi, Pb, Co, Ni, Cu, Zn, Cd, Hg, and the platinum metals (from *e.g.* a platinum crucible) all interfere. The first four of these cations can be separated as hydroxides at pH = 5; the last seven can be masked with KCN. Small amounts of Fe, Bi, and Pb can be masked with Na_2S, and larger amounts of Pb, Bi, and Sb with BAL. If it is not masked with sulphide, iron interferes even in the smallest amounts since it blocks the indicator. Alkaline earths do not interfere unless they are present in large excess. Mn, Ga, and In are titrated with the rare-earths unless they have been masked as sulphides. Y and Sc are included in the titre.

REAGENTS. Standard 0·01M–EDTA solution as titrant; Erio T; ascorbic acid; triethanolamine.

PROCEDURE. Strongly acid solutions are first brought to a pH of about 2·5 (Congo Red paper just reddened). A small spatula full of ascorbic acid is added to prevent the atmospheric oxidation of Ce, Pr, and Tb, then triethanolamine until a pH of about 7 is reached. The solution is next diluted until the concentration of lanthanons is about 10^{-3}, indicator is added, and the titration with EDTA carried on until the colour changes from red to blue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 10^{-5} gram atoms, *i.e.* to 1·3892 mg La, to 1·4013 mg Ce, etc.

REMARKS. It is important that pH = 7 at the end-point. If the pH is too low the red acid form, H_2D^-, of the indicator results and the change of colour is unsatisfactory or fails altogether. If the pH is too high precipitation takes place; furthermore any alkaline-earths present are partially included in the titre and have the effect of making the end-point long drawn out.

If alkaline earths are absent, it is also possible to carry out a back-titration at pH = 10; this is very favourable when masking with KCN those metals which form ammine complexes, for at pH = 7 too much free HCN is produced. First of all a small excess of EDTA is added to the still acid test solution. After neutralising with NaOH the solution is buffered to pH = 10, and the excess of EDTA determined by back-titration with 0·01M–$MgSO_4$. Concerning the EDTA-complexes of the lanthanons cf. refs 19, 214, and 249.

6.12. Back-titration of Zirconium with Ferric Iron Using Salicylic Acid[147]

APPLICATIONS. Determination of zirconium in the presence of practically any divalent cations. Fe, Th, Al, and rare-earths must be absent. Small amounts of sulphate ions do not interfere. In the presence of larger amounts of sulphate, as well as larger amounts of Zn, Cd, Ni, and Cu it is preferable to precipitate the zirconium as benzoate or mandelate at pH = 3, take up the precipitate in HCl, and then to start the titration procedure.

REAGENTS. Standard 0·1M–EDTA and 0·1M–$FeCl_3$, standardised against one another; solid salicylic acid; approximately M–NH_4OH; approximately M-acetic acid.

PROCEDURE. The acid test solution containing about 100 mg Zr per 100 ml is treated with a small excess of EDTA and heated to boiling. Ammonia is next added until the pH reaches 6–7 and boiling continued for 2 minutes. After cooling, 3 ml acetic acid and then 2 ml of ammonia are added; at this stage the pH should be about 5. Now 0·2 g of the solid indicator is introduced and titration carried out with the standard ferric iron until the first trace of red appears.

CALCULATION. Every ml of the difference between 0·1M–EDTA added and the volume of 0·1M–$FeCl_3$ required corresponds to 9·122 mg Zr.

REMARKS. As is always the case when the indication of an end-point depends on a reaction between Fe(III) and a phenol, the solutions must not be too dilute. However, it is still possible to carry out this titration with 0·02M solutions of titrant. The zirconium complex of EDTA is only slowly formed. Therefore it is necessary to heat the solution to start with and not to neutralise it till afterwards, otherwise a precipitate of zirconium hydroxide might come down which can only be redissolved subsequently with difficulty.

A direct titration of zirconium has also been described[80], using Eriochromecyanine RC or Alizarol Cyanon RC as indicator. The titration must be carried through within the limits of pH 1·3 and 1·5 which is very impracticable. Furthermore the end-point is rather protracted and the complexing reaction not strictly stoichieometric.

Unfortunately it is impossible to determine the excess of EDTA by back-titrating with Bi^{+3} using pyrocatechol violet, for the zirconium-indicator complex is stabler than ZrY, the zirconium complex of EDTA.

6.13. Direct Titration of Thorium with Pyrocatechol Violet [139, 236]

APPLICATIONS. Determination of Th in ores and technical products. Fe, Al, Zr, and Sb must be absent. Divalent metal cations and those of the rare-earths do not interfere.

REAGENTS. Standard 0·01M–EDTA as titrant; pyrocatechol violet (VIII); dilute ammonia.

PROCEDURE. The acidity of the test solution (which should not contain more than 5×10^{-3} moles Th per litre) is brought to about pH = 2 by adding ammonia dropwise until a test with Congo red paper no longer gives a pure blue colour. Then the pyrocatechol violet is added when the colour should be blue. If the colour should still be somewhat reddish in hue, the pH is too low; this can be corrected by a few more drops of ammonia. The solution is then warmed slightly (to about 40°C) and titrated with EDTA until the colour changes to yellow. Since hydrogen ions are liberated during the titration it is often necessary, towards the end-point, to add further drops of ammonia.

CALCULATION. Every ml of 0·01M–EDTA corresponds to 2·3212 mg Th.

REMARKS. If the solution is too cold, complex formation takes place rather too slowly and the end-point is drawn out. In place of pyrocatechol violet, the dyestuff Chromotrope 10B can be used very effectively[204]. Alizarinsulphonic acid is less satisfactory[80, 91]. Thorium can also be back-titrated with a standard solution of bismuth using pyrocatechol violet as indicator[273].

6.14. Substitution Titration for Manganese Using Erio T [71, 72]

APPLICATIONS. Determination of manganese after its separation from interfering substances, *e.g.* in a precipitate of MnO_2. Alkaline-earths, rare-earths, Ga, In, and Pb are included in the titre. Co, Ni, Zn, Cd, Hg, and the platinum metals can be masked with KCN. Al and Ti can be rendered harmless with Tiron. Bi and Sb precipitate at pH = 10 and do not interfere. The most serious interference comes from iron; small amounts of it can be masked as

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; buffer of pH = 10; 0·1M–MgY; ascorbic acid or hydroxylamine.

PROCEDURE. The test solution, obtained *e.g.* by dissolving MnO_2 in HCl, should not contain more than 15 mg Mn. Ascorbic acid, or hydroxylamine, is added to the acid solution which is warmed for a short time and then neutralised with NaOH. Next dilute to at least 100 ml, add 5 ml MgY, 2 ml buffer, several drops of indicator, and titrate to the colour change from red to blue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·5493 mg Mn.

REMARKS. In addition to the substitution titration described above, a direct titration of manganese can be carried out as follows. The above procedure is followed, but in place of the magnesium complexonate, MgY, some tartrate[71, 72] or triethanolamine[181] is added to keep the manganese in solution when it is subsequently made alkaline When tartrate is used the titration must be carried out in hot solution for the reaction of EDTA with the tartrato-complex of manganese proceeds rather slowly. Large amounts of tartrate cause bad end-points.

The back-titration of manganese also goes very well[12]. The acid solution after reduction with ascorbic acid is treated with a small excess of EDTA and then made alkaline before the excess of complexone is back-titrated with standard $MgSO_4$ or $ZnSO_4$.

For the determination of manganese in ferro-manganese, the bulk of the iron can be removed, after getting the sample into solution, by extraction with amyl acetate. Then by adding ascorbic acid, KCN, and NH_4F, residual iron and Al are masked and the titration can be carried out. If Pb is present it can be masked with BAL[118].

6.15. Direct Titration of Ferric Iron with Tiron [151, 224], Salicylic Acid, or Thiosalicylic Acid

APPLICATIONS. Rapid determination of iron in ores, soils[39, 40], siderite, cements, etc. Ti, Zr, Th, Sb, and Bi interfere. Divalent cations may be present as well as Al and the rare-earths. Ferrous iron is not included in the titre.

REAGENTS. Standard 0·1M–EDTA; Tiron (salicylic acid or thiosalicylic acid); persulphate; solid *p*-chloroaniline.

PROCEDURE. Every 100 ml of test solution should contain 20–70 mg iron and not too large an excess of hydrochloric acid. If it is feared that some of the iron may be in the divalent state, add a few crystals of persulphate and boil for a short time. Next add solid *p*-chloroaniline until no more will dissolve, and 2 ml of Tiron, and titrate the warm solution (40°C) till the blue colour goes. The end-point corresponds with the disappearance of the last trace of a greenish shade, the solution becoming a pure yellow.

The pH should be about 3, which is conveniently fixed by buffering with *p*-chloroaniline or equally well with glycine. With practice, however, it is possible to dispense with a buffer.

CALCULATION. Every ml 0·1M–EDTA corresponds to 5·585 mg Fe.

REMARKS. If very dilute solutions of EDTA are used, or if the solutions are too cold, the end-point is drawn out. If an acetate buffer is used, the concentration of acetate ion must be kept very low since otherwise the iron is transformed into an acetato-complex and the end-point is still harder to detect.

Thiocyanate ions can be used as indicator. An excellent indicator for iron[242] is Eriochromazurol S; the titration is again conducted at pH = 3. If salicylic acid is used as indicator, about 0·2 g of the solid acid are added per 100 ml solution and the titration carried out at pH = 4. Iron can also be back-titrated with a standard solution of bismuth nitrate using pyrocatechol violet as the indicator[273].

6.16. Direct Titration of Ferric Iron with Variamine Blue [65]

APPLICATIONS. As in procedure 6.15. More dilute solutions can, however, be employed and the method is therefore especially suitable for micro-titrations.

REAGENTS. Standard 0·01M–EDTA; variamine blue (XI); dilute ammonia.

PROCEDURE. The test solution should contain about 5 mg iron (in the trivalent form) per 100 ml. If excess acid is present, neutralise with ammonia to the first perceptible change of Congo red paper ($pH = 2\text{–}3$). Then add a few drops of indicator and titrate. The initial blue-violet colour goes grey just before the end-point and with the last drop of titrant changes to yellow, the colour of the iron-EDTA complex.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·5585 mg Fe.

REMARKS. The jump in redox potential at the end-point can be determined with still greater accuracy by potentiometric titration using a bright platinum electrode[179].

6.17. Direct Titration of Cobalt (II) with Murexide [55]

APPLICATIONS. Titration of cobalt after separation from interfering metals. All heavy metals interfere and only alkaline-earths may be present.

REAGENTS. Standard 0·01M–EDTA; murexide; approximately M–NH_4OH.

PROCEDURE. The acid test solution, which must not contain more than about 25 mg Co per 100 ml, is neutralised to about $pH = 6$. The indicator is next added, and in this still acid solution it assumes an orange yellow colour. The cobalt-murexide complex (probably CoH_4D^+) so formed now serves as an acid-base indicator for the subsequent neutralisation which is carried out by adding ammonia until there is a colour change to yellow ($\rightarrow CoH_2D^-$). Titration with EDTA is now conducted until there is a sharp change of colour from yellow to violet. Since the solution is only very lightly buffered, the hydrogen ions set free in the complex formation (reaction 2.4) may cause the pH to fall so low that the yellow cobalt-indicator complex again forms the orange complex. If this happens add a few more drops of ammonia and continue with the titration.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·5894 mg Co.

REMARKS. The relative stabilities of the ammine- and murexide-complexes of cobalt are such that the indicator complex is broken down by excess ammonia. The optimum conditions for obtaining a good jump in pCo at the end-point are attained by following the above procedure; for at the very low concentrations of NH_3 which prevail, the cobalt that is not complexed with EDTA is present almost exclusively as Co^{+2} ion. In this way the danger from atmospheric oxidation of the cobalt is avoided. If it were not, the very stable hexamminecobaltic complex would be formed, and this is no longer capable of reacting with EDTA.

6.18. Back-titration of Cobalt (II) with Erio T

APPLICATION. Titration of cobalt precipitates, *e.g.* cobalt pyridine thiocyanate, which have been obtained when separating Co from interfering elements.

REAGENTS. Standard 0·01M–EDTA and 0·01M–$MgSO_4$ or $ZnSO_4$; Erio T; buffer of $pH = 10$; approximately M–NaOH.

PROCEDURE. The cobalt precipitate to be determined is dissolved in acid and, after adding somewhat more than the equivalent of EDTA, neutralised with NaOH. To every 100 ml solution add 2 ml buffer, and titrate with Mg (or Zn) until the colour changes from blue to red.

CALCULATION. Every ml of the difference between the titre of EDTA added and $MgSO_4$ needed for the back-titration corresponds to 0·5894 mg Co.

REMARKS. After adding the indicator the titration must be carried out at once, otherwise there is a danger of forming the Co-Erio T complex before the end-point is reached. This complex is stabler than CoY^{-2}, but it forms more slowly. After the end-point has been reached, however, the indicator reacts quickly with the cobalt and over-titrated solutions are therefore lost[97]. Better end-points are obtained if a standard solution of manganous sulphate is used for the back-titration[282].

6.19. Direct Determination of Nickel with Murexide [117, 120, 134, 199]

APPLICATIONS. Titration of nickel after separation from interfering metals. Co, Zn, and Cd produce the most serious interference. Al and Mn, as well as small amounts of Cu and Fe can be masked with triethanolamine[167]. Larger amounts of iron must be removed[96]. If large amounts of copper are present, reduction can be effected with ascorbic acid and the subsequent titration carried out in an atmosphere of nitrogen to avoid re-oxidation. Bi and Fe(III) separate out straight away on neutralisation and after filtration no longer interfere. Rare-earths and alkaline-earths can be rendered harmless[168] with NaF. Hg is transformed into HgI_4^{-2} with iodide and no longer interferes.

REAGENTS. Standard 0·01M–EDTA as titrant; murexide; approximately M–NH_4Cl; concentrated ammonia; masking agents as required.

PROCEDURE. The acid test solution, which must not contain more than about 15 mg Ni per 100 ml is neutralised and the indicator and any necessary masking agents added. To the about neutral solution 10 ml NH_4Cl is now added. If the pH is still below 7, the indicator will show an orange yellow colour (due to the complex NiH_4D^+) and ammonia must be added dropwise until the indicator changes to a clear yellow (due to NiH_2D^-). The titration is now started and carried out until the end-point is approached. If, through lowering of the pH, the colour changes to orange again, more ammonia must be added dropwise and the titration continued. Just before the end-point the solution is made very strongly ammoniacal by adding about 10 ml concentrated ammonia, and titrated to the end-point

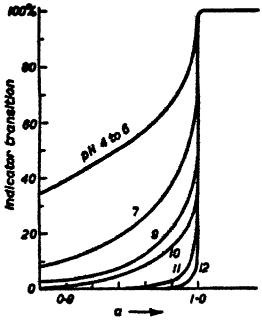


FIG. 39

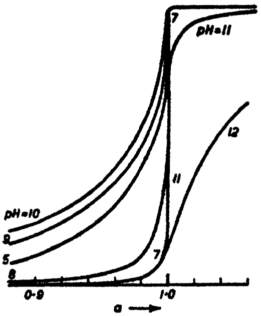


FIG. 40

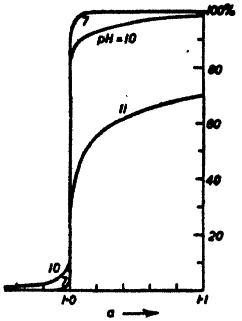


FIG. 41

FIG. 39. Colour transition of murexide (VI) during the titration of Ni at different pH values

FIG. 40. Colour transition of murexide (VI) during the titration of copper at various pH values

FIG. 41. Colour transitions of Erio T during the titration of Zn at various pH values

Attention is drawn to the fact that the scale of the abscissae in these graphs is greatly enlarged as compared with that of Figs. 30–37 which occurs with a brilliant change of colour from yellow to a bluish-violet.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·5869 mg Ni.

REMARKS. All the data needed to form a quantitative picture of this titration are known. From Figs. 7 and 24 we can construct Fig. 39 which shows that there will be a really good colour transition over the whole pH range from 7 to 12. This will, however, be at its sharpest, and at its most brilliant in strongly alkaline solution. But it is impossible to start the titration at pH = 10 to 12 as nickel hydroxide or a basic salt would precipitate. Thus we are lead to the procedure detailed above in which the titration is first carried out in neutral solution, and not until just before the end-point is the solution made strongly alkaline. There is the further practical advantage that, in the presence of nickel, murexide also acts as an acid-base indicator, permitting us to detect the neutral point. However, murexide must not be added straight away to the strongly acid test solution, for under these conditions it is rapidly hydrolysed.

6.20 Back-titration of Nickel Using Erio T

APPLICATIONS. Titration of precipitates used to separate nickel from interfering metals. *E.g.* the titration of nickel-dimethylglyoxime, or nickel-nioxime, etc.

REAGENTS. Standard 0·01M–EDTA and 0·01M–$MgSO_4$ (or $ZnSO_4$) as titrants; Erio T; approximately 2M–HCl; approximately 2M–NaOH; methyl red; buffer of pH = 10.

PROCEDURE. The precipitate of nickel dimethylglyoxime is dissolved in the least quantity of hot HCl. A small excess of EDTA is then added and the solution neutralised with NaOH to methyl red. The concentration of nickel is now brought to below 5×10^{-5}M by suitable dilution and to every 100 ml is added 2 ml buffer and a few drops of indicator. The back-titration with metal solution is then carried through to a colour change from red to blue. Over-titrated solutions are lost.

CALCULATION. Every ml of the difference in titre between 0·01M–EDTA added and 0·01M–metal used in the back-titration corresponds to 0·5869 mg Ni.

REMARKS. As in the corresponding cobalt titration (procedure 6.18), this method is feasible only because the reaction between NiY^{-2} and the indicator, Erio T, takes place very slowly so long as there is an excess of EDTA present. As soon as the end-point is reached, pNi decreases abruptly and the metal combines with Erio T to form a complex which is not decomposed if more Na_2H_2Y is added: if a standard solution of manganous sulphate is used for the back-titration, even sharper end-points are obtainable[282].

If the solution contains both Co and Ni, the above procedure yields the total concentration. Cobalt can then be precipitated with α-nitroso-β-naphthol in a second portion of the solution and extracted with chloroform; nickel remaining in solution can then be titrated as above[98]. A second possibility is to add an excess of EDTA and to oxidise cobalt with PbO_2 when the very stable complex of trivalent cobalt, CoY^-, is formed. Excess PbO_2 is then separated by filtration, and the excess of EDTA back-titrated with $MgSO_4$. On now adding KCN, a quantity of EDTA equivalent to the amount of Ni present is set free, and this can be determined in turn by titration with $MgSO_4$[170]. The EDTA complex of Co(III) does not react with KCN.

6.21. Direct Titration of Copper Using Murexide [55, 199]

APPLICATIONS. Analysis of coinage alloys[253]. Determination of copper after the removal of interfering elements. *E.g.* titration of precipitates such as CuCNS, CuS, copper-oxinate, etc. Ni, Co, Zn, Cd, and Mn must be absent. Small amounts of alkaline-earths do not interfere. Larger amounts of alkaline earths or rare-earth metals can be masked with fluoride[168]. Bi, Fe(III), and Al can easily be separated as hydroxides at pH = 5–6. Triethanolamine must not be added as a masking agent and, of course, the masking of Hg with iodide is impossible here.

REAGENTS. Standard 0·01M–EDTA as titrant; murexide; approximately M-ammonia; approximately M–NH_4Cl.

PROCEDURE. The test solution should not contain more than about 20 mg Cu per 100 ml. Acid solutions are neutralised with ammonia, but only a small excess is used so that a pH of about 8 results. If the original solution is only weakly acid, 10 ml NH_4Cl per 100 ml sample is added so that the pH does not get too high when the ammonia is subsequently added. Indicator is next added and the solution titrated with EDTA until the colour changes from yellow to violet.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·6354 mg Cu.

REMARKS. The most favourable pH for the titration can be deduced from Fig. 40, which is obtained by combining Figs. 8 and

25. In complete contrast to the corresponding nickel titration (procedure 6.19) it is preferable with copper to work at low pH values. This is because the ammine-complexes of copper are appreciably stabler than those of nickel, so that too much ammonia can decompose the copper-murexide complex again (cf. Fig. 3). High concentrations of ammonia must therefore be avoided. Naturally some ammonia must be present to keep the metal in solution, but the danger of precipitating basic copper salts, *e.g.* $CuCl_2$, $3Cu(OH)_2$, is diminished by the presence of a high concentration of NH_4^+ which keeps the pH down. Of course, ammonia is a bad buffer for the region pH = 7–8; but triethanolamine cannot be used, for its copper complexes are appreciably more stable than those with ammonia.

Copper can also be determined by a back titration with Erio T as in the case of cobalt (6.18) and nickel (6.20), and, as before, a standard solution of manganese sulphate can also be used[282]. It is preferable not to add the indicator until just before the end-point, and then to carry the titration to its conclusion without wasting a moment. This is because of the danger of forming the very stable Cu–Erio T complex which, once formed, cannot be decomposed again by EDTA. Copper can also be titrated directly using pyrocatechol violet. It is possible to work either at pH $\sim$ 6 where the colour change is from blue to yellow, or at pH $\sim$ 9 when the indicator changes from blue to violet[137].

6.22. Titration of Zinc and Cadmium Using Erio T[12, 54, 55, 116, 199, 235]

6.22.1. *Titration of Zn and Cd in the Absence of Cu, Co, and Ni.*

APPLICATIONS. Standardising solutions of zinc, or of ENTA. Determination of Zn in aluminium[53] and other copper- and nickel-free alloys[116]. Determination of zinc in Viscose precipitating baths[243]. The most serious interference in this titration come from Cu, Co, and Ni which block the indicator. At the pH necessary for the titration Fe, Ti, Al, Bi, and Pb do not remain in solution and are easily separated as hydroxides. But even the last trace of iron must be got rid of as otherwise it too would block the indicator. Small amounts of Ti and Al can be masked with Tiron or fluoride. The alkaline-earths and the rare-earth metals can also be masked with fluoride. Any manganese remaining in solution is included in the titre. Cadmium is titrated simultaneously with zinc in any case.

REAGENTS. Standard 0·01M–EDTA; Erio T; buffer of pH = 10.

PROCEDURE. Each 100 ml of the test solution should not contain more than about 25 mg Zn (or 50 mg Cd). Acid solutions are first neutralised with NaOH, if necessary after the previous removal of trivalent metals with acetate. Then to each 100 ml portion add 2 ml buffer, and a few drops of indicator, and titrate to the colour change from red to blue. The last drops of indicator should completely discharge the last trace of reddish hue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·6385 mg Zn or 1·124 mg Cd.

REMARKS. For the zinc titration we can combine curves from Figs. 9 and 21 and so obtain Fig. 41 which shows that the titration can be carried out anywhere in the pH range from 7 to 10, and with such extraordinarily sharp changes in colour that even a 0·001M solution of EDTA can be used satisfactorily. However, the solutions should not be too cold (30°– 40°C). It is not possible to work appreciably below $pH = 7$ for then the metal-free Erio T begins to occur in the red form, H_2D^-. Above $pH = 10$, the indicator transition is rather drawn out and comes a trifle late because the stability of the zinc-indicator complex is rather too high relative to that of the zinc-EDTA complex. Titration at the neutral point, $pH \sim 7$, is recommended when alkaline-earths, especially magnesium, are present. For unless their concentration is too high, they do not interfere with the zinc titration at this low pH[24, 25]. If larger amounts of magnesium are present, fluoride is added[168].

Since the stability constants for the cadmium—Erio T complexes have never been determined, the diagram corresponding to Fig. 41 cannot be drawn for the cadmium titration. It is known, however, that cadmium can be titrated over the whole pH range from 7–10. Again a pH of about 7 is advisable if the determination of Cd is to be carried out in the presence of magnesium[25].

Zinc can also be titrated using ‘zincon’ as indicator[280].

6.22.2. *Titration of Zn and Cd in Presence of Cu, Co, and Ni*[64, 116, 228]

APPLICATIONS. Determination of zinc or cadmium in brass, bronzes, and other alloys, or in ores, slags, etc. The three cations Cu, Ni, and Co are rendered harmless by adding KCN followed by formaldehyde (or chloralhydrate) which liberates Zn and Cd from their cyanide complexes and de-masks them (cf. section 4.2). The masking of other metallic impurities is dealt with in procedure 6.22.1.

The same procedure serves for the determination of Zn and Cd in cyanide solutions[182].

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; concentrated ammonia; 20% KCN; 4% formaldehyde; approximately M–NH_4Cl.

PROCEDURE. The acidic solution of the material to be analysed is neutralised with ammonia, and then a considerable excess is added. Sufficient KCN is then added for the formation of $Cu(CN)_3^{-2}$, $Co(CN)_6^{-3}$, $Ni(CN)_4^{-2}$, $Zn(CN)_4^{-2}$, and $Cd(CN)_4^{-2}$. The volume of KCN solution needed is calculated from the weight of sample taken and its approximate composition. Furthermore, it is possible to check the complete formation of the cyanide complexes of copper and nickel from the disappearance of the blue colour of the solution. The solution of cyanides is transferred to a volumetric flask and made up to a known volume. An aliquot containing about 10 mg Zn (or 15–20 mg Cd) is taken and diluted to 100 ml. A further 0·5 ml of cyanide solution is added together with a few drops of Erio T, and any alkaline earths which may be present are complexed by adding EDTA until the colour changes from red to blue. Demasking is now brought about by adding 5 ml formaldehyde, whereupon the colour of the solution returns to red. Simultaneously the pH rises and on this account sufficient NH_4Cl must be added to bring the pH back between 8 and 9. (This is easily achieved by testing drops with phenolphthalein and thymolphthalein when the first, but not the second, will show its colour.) After standing for a short time, the solution is warmed slightly, and titrated until the colour changes to blue. This gives the content of Zn and Cd.

CALCULATION. Every ml 0·01M–EDTA corresponds to 10^{-5} gram atom of either metal, *i.e.* to 0·6538 mg Zn, or to 1·124 mg Cd.

REMARKS. The cyanide complexes of zinc and cadmium have overall stability constants[21, 131] of about 10^{19}. To ensure that these metals no longer give any reaction with Erio T, their pM values at $pH = 10$ must be at least 14 (cf. Fig. 21). This can only be achieved if the concentration of free cyanide ions in solution is at least 10^{-2} (This gives approximately the following ionic concentrations: $[Zn(CN)_4] \sim 10^{-3}$; $[Zn] \sim 10^{-14}$; $[CN] \sim 10^{-2}$). Only when such an excess of cyanide has been built up is it possible to titrate any alkaline-earths that may be present, without interference from Zn and Cd.

For the next stage, the de-masking of these two metals, the cyanide concentration must be lowered to about 10^{-4}. The concentration of zinc now rises to 10^{-6} and as shown in Fig. 21, when $pZn = 6$, the Erio T occurs in the form of its zinc complex, which is red. This decrease in cyanide concentration from 10^{-2} to about 10^{-4} is obviously achieved smoothly by formaldehyde. However, the pH rises because, in consequence of reaction (4.1), HCN leaves the system, and it could only have been formed by the process:

$$CN^- + H_2O \rightarrow HCN + OH^-$$

This rise in pH can bring about the precipitation of zinc or cadmium hydroxide. The addition of NH_4Cl, however, brings the pH down again to the most favourable range.

The overall stability constant for the nickel-cyanide complex is round about 10^{27}. With a concentration of free cyanide ion of 10^{-2} we have a value for pNi of about 22; after the addition of formaldehyde, when $CN^- = 10^{-4}$ or thereabouts, pNi becomes 14. Experiments show that when the concentration of free nickel ions in solution is as low as this, the metal has not begun to react with the indicator, Erio T. However, the value of pNi must certainly not fall much lower than this for, even at a pNi value of about 9, the irreversible formation of nickel-dyestuff complexes begins. We have therefore only a limited range of conditions to work in and, in point of fact, interference is experienced if too much nickel, or too much copper, is present. The addition of formaldehyde must also be handled carefully. Too great an excess of this de-masking agent leads to the blocking of the indicator through the liberation of nickel or copper. This is almost invariably the case when the fully titrated solution is left to stand, even when the titration itself was carried through without interference.

Another possibility for the simultaneous determination of Zn and Ni is to use BAL. First of all an excess of EDTA is added and back-titration carried out with $MgSO_4$. BAL is then added when a quantity of EDTA equivalent to the zinc present is set free and can then be back-titrated with $MgSO_4$. Finally KCN is added whereupon the EDTA which had been bound to the nickel is set free and can, in its turn, be titrated with $MgSO_4$[181].

If only small amounts of zinc or cadmium are to be determined in the presence of large amounts of other metals it is best to use an extraction procedure[121, 122]. The solution to be analysed is treated with thiourea (to mask Ni and Cu), fluoride (to mask Fe) and large amounts of NH_4CNS; the thiocyanates of Zn and Cd are then extracted with *iso*butyl methyl ketone. After separation, the ketone layer is diluted with water (adding acetone to prevent the formation of two phases) and titrated directly according to procedure 2.22.1.

6.23. Titration of Zinc Using Dimethylnaphthidine [23]

APPLICATIONS. Simultaneous determination of Zn and Mg, or Zn and the sum of Ca and Mg.

REAGENTS. Standard 0·1M–EDTA as titrant; 1% $K_4Fe(CN)_6$; 1% 3:3′-dimethylnaphthidine in acetic acid; approximately M-sodium acetate; approximately M–HCl.

PROCEDURE. The test solution should be about 0·01M with respect to zinc. Acidic solutions are neutralised with NaOH (methyl red). To every 100 ml add 1 drop of ferrocyanide solution and 2–3 drops of naphthidine followed by 3 ml sodium acetate and about 0·5 ml HCl. The pH of the mixture should now lie between 5 and 6, and the colour should be a violet-red. Titration with EDTA is now carried out until the colour begins to fade perceptibly. At the end, the titrant must be added very slowly, waiting about 15 seconds between one drop and the next. With the last drop, the last trace of rose colour vanishes after the prescribed time, and the solution becomes colourless.

CALCULATION. Every ml 0·1M–EDTA corresponds to 6·358 mg Zn.

REMARKS. Buffer of pH = 10 can be added to the fully titrated solution and, using Erio T as indicator, magnesium can be determined according to procedure 6.4, or the sum of Ca and Mg by procedure 6.6.

The titration can also be carried out in the reverse sense and in this way Cu, Ni, Cd, Pb, Fe, and Al can be included. An excess of EDTA is added, the pH is brought to between 5 and 6, dimethylnaphthidine and ferrocyanide are introduced, and the excess of EDTA back-titrated with a standard solution of magnesium sulphate[73]. Zinc can be titrated at pH = 5 using 'zincon' as indicator.

6.24. Substitution Titration for Mercury Using Erio T [12, 55, 66, 199]

APPLICATIONS. Analysis of pharmaceutical products. Determination of mercury in other products after removing interfering elements. Mn, Co, Ni, Cu, Zn, Cd, In, and Pb are included in the titre (see remarks). Alkaline-earths and rare-earths can be masked with fluoride. Iron must be carefully removed as it blocks the indicator. Iodide and cyanide must be absent. Large amounts of bromide ion cause a drawn out end-point.

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; buffer of pH = 10; 0·1M–MgY.

PROCEDURE. The test solution must not contain more than about 50 mg Hg per 100 ml. Add 5 ml MgY and neutralise with NaOH (methyl red paper). Now add 2 ml of buffer and titrate with EDTA until the colour changes from red to blue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 2·006 mg Hg.

REMARKS. If other metals are present which are included in the titre, 1–2 g solid potassium iodide is added to the fully titrated solution when all the HgY^{-2} formed during the titration is transformed into HgI_4^{-2} and an equivalent amount of metal-free EDTA is liberated. The solution can then be titrated with 0·01M–$MgSO_4$ (or $ZnSO_4$) until the red colour reappears. Every ml of metal solution corresponds to 2·006 mg Hg.

Mercury lends itself very well to a back-titration[12]. A small excess of 0·01M–EDTA is added to the acid solution of the metal and after neutralisation, buffer of $pH = 10$ is added and the excess of complexone back-titrated with 0·01M–$MgSO_4$ or $ZnSO_4$.

6.25. Back-titration of Aluminium Using Erio T

APPLICATIONS. Titration of aluminium in precipitates formed when separating the metal from other elements, *e.g.* aluminium oxinate, or $Al(OH)_3$ produced by precipitation with acetate, benzoate, iodide-iodate, or thiosulphate.

REAGENTS. Standard 0·01M–EDTA and 0·01M–$ZnSO_4$ as titrants; Erio T; approximately M-ammonia.

PROCEDURE. A small excess of EDTA is run in to the acid solution of aluminium. Ammonia is added to neutralise it and bring the pH between 7 and 8 (test drops on phenol red paper). Addition of indicator should now produce a blue coloration. The titration with $ZnSO_4$ is started at once, and carried out as quickly as possible to the colour change from blue to red. The pH ought not to fall much below 7. After standing for a short time the fully titrated solution assumes a reddish-violet colour due to the formation of the aluminium-Erio T complex from the corresponding zinc complex formed initially. This reaction is irreversible and a further addition of EDTA is unable to restore the colour to blue. Even before the end-point the AlY^- reacts slowly with the dyestuff to form the Erio T-aluminium complex, and this is the reason why the titration must be carried out rapidly. Overtitrated solutions are lost because the indicator is blocked by the aluminium.

CALCULATION. Every ml of the difference between the volume of 0·01M–EDTA taken and that of the 0·01M–$ZnSO_4$ used in the back-titration corresponds to 0·2698 mg Al.

REMARKS. Mixtures of Fe(III), Al, and Be can be dealt with in the following manner. First of all the iron is titrated in acid solution according to procedure 6.16. Then the above procedure is carried through, adding an excess of EDTA but in this instance not merely neutralising with ammonia, but making more strongly ammoniacal. On boiling, $Be(OH)_2$ separates and can be determined gravimetrically[20, 164]. The filtrate from this precipitation is now brought to pH = 8 with HCl, Erio T is added, and the back-titration with $ZnSO_4$ commenced.

It is possible to titrate aluminium directly with Eriochromazurol S. The reaction is carried out at pH ~ 4 in an acetate buffer at about 80°C since the dyestuff complex is only slowly formed[241]. The end-point is recognisable from a colour change from violet to a reddish-orange. In order to make this more decisive the pH is reduced to 5 by adding sodium acetate after the end-point has been reached. The colour thereby changes to violet if too little titrant has been added and the titration must be continued. If, however, a yellow colour results at pH = 5, the solution has already passed the equivalence point and the excess of EDTA is determined by back-titration with a solution of aluminium. If iron is present as well, it can be reduced to the ferrous state with hydrazine sulphate, and so rendered harmless.

6.26. Back-titration of Aluminium with Ferric Iron Using Salicyclic Acid as Indicator[148]

APPLICATIONS. These are the same as in procedure 6.25; but in contrast the present method does not produce such a sharp end-point although it is subject to less interference from small amounts of accidental impurities such as Pt, Co, Ni, and Cu. Ti, Zr, and Th must not be present.

REAGENTS. Standard 0·1M–EDTA and 0·1M–$FeCl_3$ as titrants; solid salicylic acid; approximately M–HCl; approximately M-ammonia; approximately M-sodium acetate.

PROCEDURE. The aluminium precipitate, with a metal content of about 30–50 mg Al, is dissolved in a little HCl and treated with a slight excess of EDTA. The mixture is brought to pH ~ 6 by adding ammonia dropwise and testing with methyl red paper. The solution is then boiled for a short time. After cooling, it is diluted to at least 100 ml and 3 ml sodium acetate added. The pH should now be about 6 to 6·5. 0·2 G of the solid indicator is added and dissolved up, and then titration with the standard ferric solution is carried out until a reddish brown colour persists for a short time. During the titration the pH must not fall below 5, and to prevent this the addition of a few more drops of ammonia may be necessary.

CALCULATION. Every ml of the difference between the volumes of 0·1M–EDTA taken and 0·1M–$FeCl_3$ required for the back-titration corresponds to 2·698 mg Al.

REMARKS. The iron complex of EDTA is appreciably stabler than the corresponding aluminium complex (cf. Table 2). Therefore on reaching the equivalence point in the back-titration the following replacement reaction occurs:

$$AlY^- + Fe^{+3} \rightarrow FeY^- + Al^{+3}$$

Fortunately this reaction is a slow one, so that there can be a sufficient increase in the iron concentration at the end-point to bring about a change in the colour of the indicator. On standing, and more rapidly on warming the fully titrated solution, the brown colour of the iron salicylate fades again. The pH at the end-point must lie within narrow limits. If it is too high, the iron has to compete with the indicator on the one hand, and with hydroxide ions (formation of $FeOH^{+2}$ and $Fe(OH)_2^+$), and acetate ions (formation of acetato-complexes) on the other; the salicylic acid no longer responds sharply to changing iron content. If the pH is too low, on the other hand, the above replacement equilibrium becomes mobile, and as more iron is introduced it merely displaces aluminium from its EDTA-complex.

As in all complexometric titrations with Fe(III) and phenol-type indicators, the accuracy of the method amounts only to about 1%. The use of very dilute standard solutions cannot be recommended.

A back-titration of aluminium with thorium using Alizarin S as indicator has been described[92]. The pH is maintained between 3 and 5. The colour change is, however, very gradual; besides, thorium is rather costly for a standard solution.

6.26.1. *Back-titration of Aluminium with Zinc Using Dithizone*[248]. An excess of EDTA is added to 50 ml of the sample solution which should contain 2–15 mg of aluminium. The pH is then brought to 4·5 by adding 10 ml of an acetic acid—ammonium acetate buffer (each component is 1M). For every 50 ml of aqueous solution 40–50 ml of ethanol is added followed by 2 ml of 10^{-3} M-dithizone

(0·25 g/l. in ethanol). Titration with 0·05M–$ZnSO_4$ is then carried out until the colour changes from a greenish-violet to red.

6.27. Direct Titration of Indium Using Erio T [68, 70]

APPLICATIONS. Determination of indium in the absence of interfering elements. Iron causes the worst interference as it blocks the indicator. Alkaline-earths, the rare-earths, Mn, and Pb are included in the titre and to some extent cause the colour change at the end-point to be very gradual. Co, Ni, Zn, Cu, Hg, and Pt (from platinum crucibles) can be masked with KCN.

REAGENTS. Standard 0·01M–EDTA; Erio T; buffer of pH = 10; approximately M-sodium potassium tartrate.

PROCEDURE. To 100 ml of the test solution, which should not contain more than 20 mg of indium, add 5 ml of tartrate and then roughly neutralise to methyl red (test-paper). Add 2 ml of buffer and heat to boiling; add the indicator, and titrate hot to a colour change from red to blue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 1·1476 mg In.

REMARKS. The complexing reaction proceeds very slowly indeed with indium, and it is therefore essential to carry out the titration with the solution hot. After the first change in colour, the solution must be boiled up again and one minute allowed to elapse. Very often the red colour returns showing that a further drop of titrant is needed.

Indium can also and preferably be determined by a substitution titration or by a back-titration. The corresponding titrations cannot be carried out with gallium. On the other hand, gallium can be dealt with by adding excess of EDTA and back-titrating[69]. Back-titration with $Bi(NO_3)_3$ using pyrocatechol violet as indicator proves very satisfactory for gallium and indium[273].

6.28. Substitution Titration for Thallium Using Erio T [59]

APPLICATIONS. Titration of thallium in a precipitate of TlI. Any silver separating as AgI with the TlI does not interfere. Lead must be separated, which is most easily effected by precipitating the thallium iodide in the presence of EDTA in not too strongly acid solution; lead then remains in solution[164].

REAGENTS. Standard 0·01M–EDTA as titrant; Erio T; buffer of pH = 10; fuming nitric acid; approximately M–NaOH; approximately 0·1M–MgY.

PROCEDURE. The precipitate of thallium iodide (containing about 10–30 mg Tl) is filtered off, washed with KI solution, and dissolved in a few drops of HNO_3; the resulting iodine and nitrous fumes are driven off by evaporating almost to dryness. The residue is taken up in water and, after dilution to 100 ml, 5 ml MgY are added. The solution is neutralised with NaOH, and 2 ml of buffer and a few drops of indicator are introduced. Titration with EDTA is then carried out until the colour changes from red to a blue free from the last trace of reddish hue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 2·044 mg Tl.

6.29. Titration of Lead Using Erio T

6.29.1. *Direct Titration of Lead Using Tartrate or Triethanolamine*[56, 77]

APPLICATIONS. Determination of lead in ores, alloys[123, 161], pigments[54], and other products. Iron causes the gravest interference by blocking the indicator. Co, Ni, Cu, Zn, Cd, Hg, and Pt (from crucibles) can be masked with KCN. Alkaline-earths, the rare-earth metals, Mn and In are included in the titre. Bi, Sb, and Al do not interfere, apart from the turbidity caused by their hydroxides when insufficient tartrate is present. In the presence of interfering elements, or those which are titrated simultaneously, the lead is first separated as $PbSO_4$ and this precipitate taken for the complexometric titration.

REAGENTS. Standard 0·01M–EDTA; Erio T; buffer of $pH = 10$; approximately M-sodium potassium tartrate, or triethanolamine 1:4; KCN as a masking agent if required.

PROCEDURE. The test solution should contain not more than about 30 mg Pb per 100 ml. It is treated with 5 ml tartrate or triethanolamine (or the precipitated $PbSO_4$ is dissolved in tartrate or triethanolamine) and approximately neutralised with NaOH. If necessary, masking agent is added at this stage. After adding 2 ml buffer and the indicator, the titration with EDTA is carried out until the colour changes from red to blue. The solution must not be too cold (about 40°C) and the last trace of a reddish hue should vanish with the last drop of titrant.

CALCULATION. Every ml 0·01M–EDTA corresponds to 2·0721 mg Pb.

6.29.2. *Substitution Titration for Lead Using Erio T*[54]

APPLICATIONS. As in procedure 6.29.1.

REAGENTS. Standard 0·01M–EDTA; Erio T; buffer of $pH = 10$; approximately 0·01M–MgY; approximately M–NaOH.

PROCEDURE. The test solution, which should not contain more than 30 mg Pb per 100 ml, is treated with 5 ml MgY (in the case of $PbSO_4$ this is dissolved directly in MgY) and roughly neutralised with NaOH. Masking agent is added at this stage if required. Then 2 ml buffer, and a few drops of indicator are added, and the titration carried out to the change of colour from red to blue.

CALCULATION. Every ml 0·01M–EDTA corresponds to 2·0721 mg Pb.

REMARKS. The back-titration of lead is also a good method[12]. A small excess of EDTA is added, the solution neutralised, buffer and indicator added, and titration effected with $MgSO_4$ or $ZnSO_4$.

Lead and manganese can be determined simultaneously by first finding the total concentration using MgY as above. When the end-point has been reached BAL is added, whereupon an amount of EDTA equivalent to all the lead present is set free and can be titrated[296].

6.30. Direct Titration of Bismuth Using Pyrocatechol Violet[188]

APPLICATIONS. Determination of Bi in alloys, ores, pharmaceutical preparations, etc. Fe, Th, Zr, Sb, and Hg interfere and must be removed. Pb, Mn, Co, Ni, Cu, Zn, Cd, Al, the alkaline-earths, and the rare-earths do not interfere. The effect of chloride is discussed below (cf. REMARKS).

REAGENTS. Standard 0·01M–EDTA as titrant; pyrocatechol violet (VIII); approximately M-ammonia.

PROCEDURE. The sample to be analysed is dissolved in a little HNO_3 and the excess of solvent fumed off thoroughly. Water is added to give a solution containing not more than about 20–30 mg Bi per 100 ml. On now adding indicator a pure blue colour should result. Should it be violet or reddish, this means that the acidity is too high, and ammonia is added dropwise until the colour becomes a pure blue. This will be the case when the pH is about 2·5. Titration with EDTA is now carried out until there is a very sharp change in colour to yellow. Since hydrogen ions are liberated during the complex-forming reaction (2.4), the pH may fall too low again during the titration; this is corrected by adding another drop of ammonia.

Above $pH = 4$ the change of colour is directly from blue to yellow. But if the acidity is somewhat greater, at say $pH = 3$, a violet transition colour occurs just before the end-point. This only persists while a few drops of titrant are being added and with the last drop it changes to yellow with quite extraordinary sharpness.

CALCULATION. Every ml 0·01M–EDTA corresponds to 2·0900 mg Bi.

REMARKS. If chloride is present (Br^- and I^- are removed by fuming down with nitric acid) there is trouble in attaining the best pH region since BiOCl always separates out. In such a case it is better to carry out the titration in the reverse order, *i.e.* to perform a back-titration. A small excess of EDTA is added to the acid test solution and the pH adjusted to between 2·5 and 3. The excess of complexone is then back-titrated with 0·01M–$Bi(NO_3)_3$. The titration described above is far superior to the back-titration of Bi with Alizarin S and thorium[93].

There is also the possibility of using iodide ions[37] or thiourea[81] as indicator in this titration.

A standard solution of $Bi(NO_3)_3$ is also very suitable for back-titration procedures using pyrocatechol violet as indicator. Fe(III), Zr, Th, and Bi can be determined in this way[273].

6.31. Indirect Titration of Sodium [57]

The method depends on the preliminary precipitation of the alkali metal as sodium zinc uranyl acetate, and the subsequent determination of the zinc contained in this.

APPLICATIONS. Generally useful for determinations of sodium. The procedures for precipitation of sodium as $NaZn(UO_2)_3(CH_3COO)_9$ are followed closely.

REAGENTS. Zinc uranyl acetate, and all the solutions prescribed for washing the precipitate of the triple acetate; standard 0·01M–EDTA as titrant; buffer of pH = 10; approximately M–HCl; approximately M–$(NH_4)_2CO_3$; Erio T.

PROCEDURE. The filter carrying the washed precipitate of sodium zinc uranyl acetate (which should contain about 5 mg Na) is transferred to a beaker and moistened with 3–5 ml HCl. 50 Ml water are added and the suspension boiled up and filtered. After washing, the filtrate, which should now have a volume of about 100 ml, is neutralised with ammonium carbonate and a small excess is then added to hold the uranium in solution as the carbonato-complex. 2 Ml buffer, and indicator, are added to the pale yellow solution which is then titrated with EDTA. On account of the presence of uranium mixed colours result, with a yellowish-red before the end-point and a greenish-blue in the fully titrated solution.

CALCULATION. Every ml 0·01M–EDTA corresponds to 0·230 mg Na.

REMARKS. The titration for zinc can be carried out anywhere in the pH range from 7 to 10. It is therefore insensitive to the amount of ammonium ion present so that quite large amounts of HCl can be used in dissolving up the precipitate; in this case it is quite unnecessary to add any buffer later on.

6.32. Indirect Titration of Phosphate [74, 75]

Phosphate is first precipitated as $Mg(NH_4)PO_4, 6H_2O$. This can be carried out, even in the presence of a variety of foreign metals, by first transforming these into their complexes with EDTA and then making alkaline with ammonia and adding magnesia mixture[109, 175]. The precipitate is then dissolved in acid, an excess of standard EDTA added, the pH brought to 10, and the excess of complexone back-titrated with $MgSO_4$.

APPLICATIONS. Determination of phosphate in soils, minerals, fertilisers, technical products, biological materials, etc. Alkaline-earths, rare-earth metals, Fe, Al, Mn, Co, Ni, Cu, Zn, Cd, Hg, and Bi do not interfere.

REAGENTS. Approximately 2M–EDTA as a masking agent; approximately M–$MgSO_4$ as a precipitant; concentrated ammonia; standard 0·1M–EDTA and 0·1M–$MgSO_4$ as titrants, standardised one against the other; Erio T; approximately M–HCl; approximately M–NaOH; buffer of pH = 10.

PROCEDURE. The acidic solution of the sample to be determined should not contain more than about 350 mg PO_4. It is treated with sufficient 2M–EDTA to form complexes with all the polyvalent metal cations contained in it. An excess of M–$MgSO_4$ is then added, and the boiling solution treated slowly dropwise with concentrated ammonia. After the amount of precipitate no longer increases, a further small excess of ammonia is added, and the solution allowed to stand for several hours. For very accurate results, a double precipitation is carried out. Finally, the precipitate is collected and thoroughly washed with M–NH_4OH.

The filter and precipitate is transferred to a beaker and treated with 10 ml M–HCl. About 50 ml water is added, the suspension is boiled up, filtered afresh, and the residue well washed. The filtrate and washings should now occupy a volume of about 150–200 ml. A small excess of the standard solution of 0·1M–EDTA is now added and, after neutralisation with M–NaOH, 2–4 ml of buffer and indicator are added. Back-titration with standard $MgSO_4$ solution is then carried out until the colour changes from blue to red.

CALCULATION. Every ml of the difference between the volumes of 0·1M–EDTA taken and that of the 0·1M–$MgSO_4$ used in the back-titration corresponds to 3·098 mg P, or to 9·498 mg PO_4, or to 7·098 mg P_2O_5.

REMARKS. If the amount of phosphate to be determined is very small it can be titrated directly. The solution of the precipitate in HCl is neutralised and buffer added without any immediate precipitation occurring. The supersaturated solution of $Mg(NH_4)PO_4$ can then be titrated directly with EDTA; for such small amounts it is best to use 0·01M–EDTA.

The basic principles of the indirect phosphate titration apply equally to the volumetric determination of pyrophosphate[279, 292] and sulphide[284].

6.33. Indirect Determination of Sulphate [5]

The sulphate to be determined is precipitated by a small excess of $BaCl_2$ and the excess subsequently determined by a complexometric titration using procedures 6.10 or 6.7.1.

APPLICATIONS. Determination of sulphur in organic substances after decomposition by Carius' or Wurzschmitt's method. Polyvalent cations must be absent. It is very often possible to remove these by running the test solution through a cation exchange resin in the hydrogen-ion form.

REAGENTS. Standard 0·01M–EDTA and 0·01 $BaCl_2$, standardised one against the other; metalphthalein-naphthol green; concentrated ammonia; approximately M–NaOH; ethanol.

PROCEDURE. A portion of the test solution containing about 20–50 mg sulphate ion is slightly acidified and treated slowly with 0·01M–$BaCl_2$ which is added dropwise to the hot solution until a slight excess is present; every ml barium solution corresponds to about 1 mg of sulphate. After having been left to stand for some time on the water-bath to allow the precipitate to coagulate thoroughly, the solution is cooled, and neutralised with NaOH. The volume at this stage should be about 100 ml. 5–10 Ml of ammonia and 0·3 ml of indicator are added, and the red suspension titrated with 0·01M–EDTA until the red colour suddenly fades. After the end-point has been reached a small excess of EDTA is added since it is possible to determine the equivalent point more accurately by back-titration in an alcoholic medium. The total volume of the solution is estimated roughly and an equal volume of ethyl alcohol is added whereupon the colour becomes greenish. The second back-titration with 0·01M–$BaCl_2$ is then carried out, the end-point being easily characterised by the sudden appearance of a red colour.

CALCULATION. The difference between the total volume of 0·01M–$BaCl_2$ used and that of the 0·01M–EDTA is calculated. Every ml of this difference corresponds to 0·321 mg S, or to 0·801 mg SO_3, or to 0·961 mg SO_4.

REMARKS. Compare those attached to procedure 6.10. The back-titration of the excess of barium in the suspension of $BaSO_4$ can also be carried out according to procedure 6.7.2.

Belcher and West state that precipitated $BaSO_4$ can also be dissolved in ammoniacal EDTA, the excess being back-titrated with $MgCl_2$ or $ZnSO_4$[9, 111].

Chromate can be determined in essentially the same way as sulphate, *i.e.* by adding a known amount of Ba and determining the excess by a back-titration[278].

6.34. Indirect Determination of Cyanide [108]

An excess of a solution of accurately known nickel content is added to the solution of cyanide which is to be determined. The complex ion $Ni(CN)_4^{-2}$ is formed, and the excess of nickel is determined by procedure 6.19.

APPLICATIONS. Determination of the cyanide content of alkali cyanides, of prussic acid, and of electro-plating baths. In alkaline cyanide solutions which contain copper, nickel, silver, or gold, only the excess of cyanide is determined. Cd, Zn, and Hg interfere.

REAGENTS. Solutions of 0·01M–EDTA and 0·01M–$NiSO_4$ which have been standardised one against the other; murexide; concentrated ammonia; approximately M–NH_4Cl.

PROCEDURE. 50 Ml of the 0·01M–$NiSO_4$ solution is mixed with 10 ml concentrated ammonia and 10 ml ammonium chloride, and an aliquot of the test solution (containing about 40 mg of cyanide ion) is introduced. On adding the indicator a yellow colour should result, and without loss of time the titration with 0·01M–EDTA is carried out until the colour changes to violet.

CALCULATION. The difference between the volume of 0·01M–$NiSO_4$ taken and that of the 0·01M–EDTA used in the back-titration is calculated. Every ml of this difference corresponds to 1·040 mg CN.

REMARKS. If the cyanide solution is added directly to the neutral nickel sulphate solution there is a danger of forming the sparingly soluble cyanide, $Ni[Ni(CN)_4]$. Thus it is desirable to make the solution strongly ammoniacal from the beginning, as described above. But, to be sure, ammoniacal solutions of nickel are not indefinitely stable, for hydroxide can precipitate out eventually. Therefore the titration is carried out as soon as possible after the solutions have been mixed.

A rough calculation shows that the stability of the tetra-cyano-nickelate ion is just high enough to make this titration possible. To bring about the colour change of murexide at pH = 10 the value of pNi must be at least 11 (cf. Fig. 24). Let us assume that the concentration of the nickelocyanide complex at the end-point is about 10^{-3} moles per litre. Then from the overall stability constant of 10^{27} we calculate a concentration of free cyanide ions

$$[CN^-] = 2 \times 10^{-5}$$

This is about 0·5% of the total concentration of cyanide (4×10^{-3}) implying that, at the end-point where pNi = 11, the EDTA has already displaced 0·5% of the total cyanide from its complex with nickel. But it is probable, anyway, that all these equilibria are only slowly established, so that there is time to complete the titration before the nickel is displaced by EDTA from its cyanide complex.

6.35. Indirect Titration of Silver, Halides [58, 76], and Thiocyanate

The silver ion in the solution to be analysed, or a solid silver salt is allowed to react with $Ni(CN)_4^{-2}$ ions whereby an equivalent amount of nickel is set free which can be determined with EDTA, using murexide as indicator (cf. section 2.2.5.4.)

APPLICATIONS. Titration of silver after precipitation as AgCl; titration of chloride, bromide, iodide, or thiocyanate after precipitation as AgCl, AgBr, AgI, or AgCNS. Analysis of silver salts such as $AgNO_3$, Ag_2SO_4, silver acetate, $AgBrO_3$, $AgIO_3$, etc. Titration of copper and silver in coinage alloys. After the sample has been got into solution, HCl is added to precipitate AgCl and the copper is titrated. Addition of $Ni(CN)_4^{-2}$ causes the liberation of Ni equivalent to the silver present[253].

REAGENTS. Solid potassium cyanonickelate, $K_2Ni(CN)_4$ (for its preparation cf. Flaschka, ref. 58); standard 0·01M–EDTA as titrant; murexide; concentrated ammonia; approximately M–NH_4Cl.

PROCEDURE. The solid silver salt to be analysed (which should contain about 100 mg Ag) is treated with 10 ml ammonia and 10 ml NH_4Cl. On adding 0·2 g of potassium cyanonickelate it should go into solution though if necessary this process may be assisted by warming (*e.g.* with AgI). Dilute to 100–200 ml, add the indicator, and titrate with EDTA until the colour changes from yellow to violet.

CALCULATION. Every ml 0·01M–EDTA corresponds to 2·158 mg Ag, to 0·709 mg Cl, to 1·598 mg Br, to 2·538 mg I, or to 1·16 mg CNS.

REMARKS. The overall stability constant of the complex ion $Ni(CN)_4^{-2}$ is 10^{27}, and that of $Ag(CN)_2^-$ is 10^{21} (cf. ref. 82). From these figures we deduce that the equilibrium constant for the reaction:

$$2Ag^+ + Ni(CN)_4^{-2} \rightleftharpoons 2Ag(CN)_2^- + Ni^{+2}$$

is 10^{15}, *i.e.* the reaction proceeds practically completely to the right. If the nickel complex is present in excess, the concentration of free silver ions drops to about 10^{-10} which is low enough to ensure the dissolution of such sparingly soluble salts as AgCl, AgBr, and AgCNS, though not of AgI. Moreover silver cyanide cannot precipitate out, though there is a danger of forming the sparingly soluble nickel cyanide:

$$Ni^{+2} + Ni(CN)_4^{-2} \rightarrow Ni[Ni(CN)_4]$$

To overcome these difficulties, sufficient ammonia is added to transform the free nickel ions into ammine complexes. At the same time any silver which is not bound to CN^- is transformed into the ammine complex, $Ag(NH_3)^{2+}$. If the concentration of ammonia is taken as 1, which is about the right figure after dilution has been carried out according to the above procedure, the equilbrium constant for the replacement reaction now assumes the following value:

$$\frac{[Ni]'[Ag(CN)_2]^2}{[Ag]'^2[Ni(CN)_4]} = 2{\cdot}6 \times 10^9$$

[Ni]′ and [Ag]′ denote the total concentration of nickel and silver respectively that is not bound to cyanide. Explicitly:

$$[Ni]' = \sum_{n=0}^{6} [Ni(NH_3)_n] \cong 2{\cdot}6 \times 10^8\,[Ni]$$

$$[Ag]' = \sum_{n=0}^{2} [Ag(NH_3)_n] \cong 10^7\,[Ag]$$

Hence in the presence of excess cyanonickelate ion, [Ag]′ drops to about 10^{-8}, and the concentration of free silver ions, [Ag], to 10^{-15};

this is low enough to ensure the dissolution of even the very sparingly soluble silver iodide.

6.36. Indirect Titration of Palladium [62]

The principle of the procedure 6.35 for silver can be applied to the determination of palladium. Since the tetracyanopalladium complex, $Pd(CN)_4^{-2}$, is stabler than the corresponding complex of nickel, the latter is set free when an excess of tetracyanonickelate is allowed to react with palladium (II) chloride. The nickel thus set free is titrated as before with EDTA (cf. section 2.2.5.4.)

APPLICATIONS. Content of palladium preparations, *e.g.* palladium chloride, palladium metal, palladium catalysts, etc. If metallic Pd is to be determined it must first be taken up in *aqua regia* and the solution fumed down several times with concentrated HCl to bring the palladium into the divalent form.

REAGENTS. Solid $K_2Ni(CN)_4$ (for preparation cf. Flaschka, ref. 58); standard 0·01M–EDTA as titrant; murexide; concentrated ammonia.

PROCEDURE. The test solution must contain palladium in the divalent state, in amount not exceeding about 20 mg. Add 10 ml concentrated ammonia and 0·2 g potassium cyanonickelate, warm for a short time, dilute to 100–200 ml, introduce the indicator, and titrate with EDTA until the colour changes from yellow to violet.

CALCULATION. Every ml 0·01M–EDTA corresponds to 1·067 mg Pd.

REMARKS. Gold and platinum, but not Ir, Rh, and Ru, can be determined in the same way[119]. Palladium can also be determined by back-titration with a standard solution of a mercuric salt, using Erio T as indicator[136].

CHAPTER SEVEN

Concluding Remarks

7.1. The advantages and possible practical applications of complexometric titrations have been pointed out in the preceding pages. We ought now to pause and consider the lacunae, for there is a whole range of metal cations which still cannot be determined complexometrically. Moreover, it is often very difficult or impossible to devise specific titrations for certain individual components in mixtures. To remedy these defects we must consider introducing other chelating agents to act as titrants, and look round for metal indicators and masking agents of novel types.

Complexometric methods are lacking for the alkali metals in particular, and for the small or highly charged cations of the elements Be, B, Ti, Ge, Nb, and Ta, for the platinum metals and the elements As, Sb, Sn, Mo, and W which form thio-complexes, and, of course, for anions.

Methods for chromium and vanadium have not yet been worked out in detail. But without doubt a substitution titration could be used for Cr^{+3} as well as for V^{+3} and VO^{+2} since the stability constants of the complexes CrY^-, VY^-, and VOY^{-2} are 10^{23}, 10^{25}, and 10^{18} respectively[222]. Complications arise from the colours of these ions themselves and those of their complexes with EDTA. The complex between chromium and EDTA is formed very slowly, so that after adding an excess of MgY^{-2} the mixture must be warmed for some considerable time.

Of the alkali metals it can be said that, in principle at least, their cations should be able to form complexonates. The most stable complexes of the alkali metals yet encountered are those with uramildiacetic acid[220] where the stability constants for the lithium and sodium complexes, LiZ^{-2} and NaZ^{-2}, are about 10^5 and 10^3 respectively. Unfortunately, equilibrium constants of this order are too low for complexometric titrations where the complex formed should have a stability constant of at least 10^7. There seems little hope of finding substances which will be able to form complexes as strong as this with alkali metal cations.

Cations of the elements Be, B, Ti, Ge, Nb, and Ta are found to combine with hydroxyl ions in preference to the anion of a complexone, thereby forming giant lattices (whence precipitation) or characteristic hydroxy-complexes. With titantium, the formation of a complex with EDTA can be observed in acid solution. But in general, these metals have only a slight tendency to coordinate through basic nitrogen atoms; furthermore the carboxylate groups of complexones are manifestly too bulky for very small cations. Polyphenols would be intrinsically more favourable as complexing partners in such cases. However, the rigid structure of the aromatic ring system prevents more than two phenolic hydroxyl groups being introduced into a molecule in such a way that their oxygen atoms can coordinate simultaneously to the metal cation. The best chelating agents for Be, B, Ti, Ge, Nb, and Ta are therefore the derivatives of pyrocatechol (*e.g.* Tiron) or 1:8-dihydroxynaphthalene (*e.g.* chromotropic acid) and these have, in fact, already been selected as masking agents for these metals. The use of such di-phenols as titrating agents looks definitely promising; but the slowness of complex formation may cause difficulties.

Among the platinum metals and the elements As, Sb, Sn, Mo, and W which form thio-complexes, chelating agents which can coordinate to the metal through sulphur (as in mercaptans) or through phosphorus (as with alkylphosphines) would certainly be effective. The reaction between tin and 1:2-dimercaptobenzene is well known*, and a compound like tris-(β-mercaptoethyl)-phosphine $P(CH_2CH_2\cdot SH)_3$, analogous to NITA (III) or to triethanolamine, $N(CH_2CH_2\cdot OH)_3$, should certainly prove to be an exceptionally good complexing partner for the whole group. However, mercaptans and phosphines are very sensitive to atmospheric oxidation, and this would prove a serious drawback to their practical use in volumetric analysis.

Finally, if we wished to bind anions with a chelating molecule we should have to furnish it with electrophilic groups, whereas all the complexing agents known hitherto contain nucleophilic atoms such as N, O, S, etc., which naturally can serve as ligands only for positive ions. Mercury is probably the only electrophilic ion which could be attached to carbon. Certainly, alkyl mercuric nitrates can bind halogens, and the stability of a complex of this type ought to increase considerably with a di-mercuric or poly-mercuric compound. Such a reagent would probably combine not only with halogens but with other anions as well.

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* Cf. G. Schwarzenbach, *Helv. Chim. Acta*, 1932, 15, 1480.

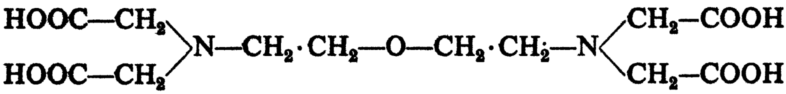
7.2. This brief review will have made it clear why the complexones have assumed such an important role in analytical chemistry. Practical considerations limit our choice of ligand atoms to O and N. The N has to be introduced in the form of an aliphatic amine, which is more strongly basic than an aromatic amine[226]. With O, virtually only the oxygen of a carboxyl group comes into question, for the oxygen of an ether, or that of an alcoholic hydroxyl group is too feebly basic (nucleophilic). To be sure, phenolate ions ought to prove very suitable; but the oxygen atoms have to be attached to an aromatic ring-system which severely restricts their use in a chelating agent on purely stereochemical grounds[205]. Furthermore, whereas doubly bound oxygen can only be introduced as a terminal group, trivalent nitrogen can serve either as a bridging atom or as a branching point which holds together different parts of the complexing agent. These considerations lead inevitably to the structural features found in the aminopolycarboxylic acids.

Of the various complexones, EDTA has the best possible structure; for in its anion there are six ligand atoms, so that it corresponds with the coordination number most frequently encountered among the metals and, in addition, it forms five-membered chelate rings on coordination[110]. Four-membered rings would be strained, and the chelate effect is significantly smaller with six-membered rings[198]. An alternative arrangement of the groups, such as in derivatives of amino-malonic acid, is less favourable on steric grounds[219].

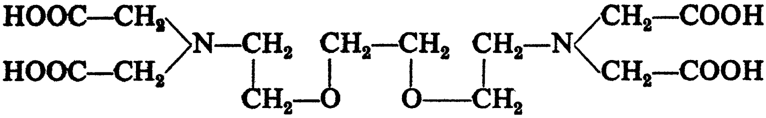
Among the many substances investigated by us in Zürich, only three have shown outstanding advantages in certain features when compared with EDTA. They are the tetra-acetates derived from two amino-ethers and from 1:2-diamino*cyclo*hexane; they all originated in the laboratories of the firm J. R. Geigy & Co., of Bâle.

The stability constants of a number of complexes formed by these three tetra-acetates are collected in Table 7, with values for EDTA for comparison.

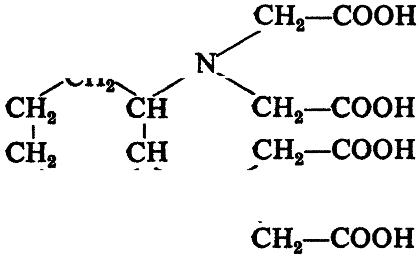
It will be seen that the two complexones, (XV) and (XVI), derived from ethers, have a greater tendency to combine with the heavier alkaline-earth metals than with magnesium. This should afford certain advantages in a substitution reaction for Sr and Ba, or in the titration of these metals together with magnesium using Erio T as indicator (procedure 6.7). ETHENTA (XV) is particularly promising in this connection for the barium complex is almost as stable as that of magnesium—the metal to which the indicator responds. With GLENTA (XVI), circumstances are less favourable. To be sure the barium complex is now still more stable; but the stability of the magnesium complex is now too low to produce a satisfactory colour-change at the end-point.



Di(2-aminoethyl) ether-NNN′N′-tetra-acetic acid
(XV; ETHENTA)



Di-(2-aminoethyl) ethyleneglycol-NNN′N′-tetra-acetic acid
(XVI; GLENTA)



1:2-Diamino*cyclo*hexanetetra-acetic acid
(XVII; DCYTA; Complexone IV)

The ether-complexones show no points of advantage for titrations of the heavy metals; on the contrary, they suffer from the disability that the apparent stability constants fall off very rapidly with decreasing pH because their acid dissociation constants, K_{H_2Z}, are significantly larger than that of EDTA.

The complexes of DCYTA (XVII) are for the most part considerably more stable than those of EDTA (IV); any advantages are, however, less real than might appear since K_{HZ} is greater too. Přibil has proposed DCYTA for use in complexometric titrations[182] and it has been named Complexone IV. However, its advantages over EDTA are certainly small. It is a characteristic feature of the homocyclic tetra-acetic acid DCYTA that its metal complexes form more slowly than those of EDTA so that the end-point in a titration tends to be drawn out and the titration must therefore be carried out slowly. This sluggishness in the formation, and also in the dissociation, of complexes ought to work out advantageously in back-titrations, *e.g.* in procedures 6.18 and 6.20, and in the corresponding back-titration for copper using Erio T as indicator. We may likewise anticipate some advantages from using DCYTA in certain separation procedures which depend on the fact that the complexes of the metals to be separated dissociate at different speeds to liberate first the metal which is to be precipitated—much as CoS is precipitated from a mixture of the complexes of Co and Ni with EDTA by adding ammonium sulphide and calcium ions, due to the slower rate of decomposition of the nickel-EDTA complex.

TABLE 7

Stability constants of complexes, defined by equation (1.8), valid for 20°C and an ionic strength $\mu = 0{\cdot}1$

Cation	log K_{MZ} for ETHENTA (XV)	log K_{MZ} for GLENTA (XVI)	log K_{MZ} for DCYTA (XVII)	log K_{MZ} for EDTA (IV)
H$^+$ $n = 1$	9·49	9·43	11·70	10·26
$n = 2$	8·82	8·85	6·12	6·16
$n = 3$	2·67	2·68	3·52	2·67
$n = 4$	1·9	2·0	2·4	2·0
Mg^{+2}	8·3	5·2	10·3	8·69
Ca^{+2}	10·0	11·0	12·1	10·70
Ba^{+2}	8·2	8·4	8·0	7·76
Mn^{+2}	13·2	—	16·8	13·79
Co^{+2}	—	—	18·9	16·31
Cu^{+2}	17·8	—	21·3	18·8
Zn^{+2}	15·3	—	18·7	16·5
Cd^{+2}	17·8	—	19·2	16·46
Pb^{+2}	—	—	19·7	18·02
Al^{+3}	—	—	17·6	16·13
Rare-earths	—	—	16·2 to 21·5	15·5 to 19·8

7.3. There is a very definite shortage of metal indicators. Of the familiar reagents now in use for the qualitative detection of metals by colour reactions or for their spectrophotometric determination, the molecular extinction coefficient is frequently insufficiently large[100, 101] or the coloured complexes do not release their metal when treated with EDTA. Sufficient intensity of absorption is only attained if the indicator has the typical resonance system of a true dyestuff* and is also able to combine with metal ions. The idea of introducing specific groupings capable of chelating metal ions into the structure of known acid-base indicators has been successful in the case of metalphthalein VII, and pyrocatechol violet (VIII). The introduction of a methyl-imino-diacetato group into nitrophenol[206] gave a compound which certainly showed the colour effects predicted theoretically; but the range of colour changes were insufficiently striking and the stability of the indicator-metal complexes too low for practical purposes. Nevertheless the application of this principle in the synthesis of new metal indicators will surely bear more fruit before long.

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* G. Schwarzenbach, *Z. Electrochem.*, 1951, 47, 40.

7.4. So far as masking agents of novel types are concerned, there are still many possibilities as yet unexplored. Polyalcohols, hydroxy-acids, amino-acids, polyamines, amino-alcohols, mercaptans, and other compounds will have to be tried out. Very little can be said about the results to be expected until the formation constants of the resulting metal complexes are known. New quantitative measurements are clearly of the utmost importance for any further advances in complexometry.

Key to Reference Abbreviations

REFERENCE	FULL TITLE
Acta Chem. Scand.	Acta Chemica Scandinavica
An. Soc. esp. Fís. Quím.	Anales de la Sociedad española de física y química
Anal. Chem.	Analytical Chemistry
Anal. Chim. Acta	Analytica Chimica Acta
Analyst	The Analyst
Angew. Chem.	Angewandte Chemie
Chem. Abs.	Chemical Abstracts
Chem. Analyst	The Chemist Analyst
Chem. and Industry	Chemistry and Industry
Chem. Listy	Chemické Listy
Coll. Czech Chem. Commun.	Collection of Czechoslovak Chemical Communications
Chim. anal.	Chimie analytique
Chimia (Switz.)	Chimia (Switzerland)
Chem. Ind. (Düsseldorf)	Chemische Industrie (Düsseldorf)
Chem. Rev.	Chemical Reviews
Chem. Weekblad	Chemisch Weekblad
Electroplating and Metal Finishing	Electroplating and Metal Finishing
Fette u. Seifen	Fette und Seifen einschliesslich der Anstrichmittel
Finska Kemistamfundets Medd.	Finska Kemistamfundets Meddelanden (Suomen Kemistiseuran Tiedonantoja).
Fortschr. chem. Forsch.	Fortschritte der chemischen Forschung
Glas-Email-Keramo-Tech.	Glass-Email-Keramo-Technik
Helv. Chim. Acta	Helvetica Chimica Acta
Inf. Quim. Anal.	Informacion de Quimica Analytica Pura y Aplicada a la Industria.
J. Am. Chem. Soc.	Journal of the American Chemical Society
J. Biol. Chem.	Journal of Biological Chemistry
J. Am. Water. Works Assoc.	Journal of the American Water Works Association
J. Am. Pharm. Assoc.	Journal of the American Pharmaceutical Association
J. Brit. Cast Iron Res.	British Cast Iron Research. Journal of Research and Development
J. Chem. Soc.	Journal of the Chemical Society (London)
J. Chem. Soc. Japan	Journal of the Chemical Society of Japan
J. chim. phys.	Journal de chimie physique

REFERENCE	FULL TITLE
J. Inst. Water Engrs.	Journal of the Institution of Water Engineers
J. Lab. Clin. Med.	Journal of Laboratory and Clinical Medicine
J. Sci. Ind. Res. India	Journal of Scientific and Industrial Research, India
Japan Analyst	Japan Analyst
Magyar Kém. Folyóirat	Magyar Kémiai Folyóirat
Metal Finishing	Metal Finishing
Metallurgia	Metallurgia (The British Journal of Metals)
Mikrochim. Acta	Mikrochimica Acta
Mikrochemie ver. Mikrochim. Acta	Mikrochemie vereinigt mit Mikrochimica Acta
Nature	Nature (London)
Naturwiss.	Naturwissenschaften
Österr. Chem. Ztg.	Österreichische Chemiker-Zeitung.
Österr. Wasserwirtsch.	Österreichische Wasserwirtschaft.
Power	Power
Proc. Soc. Expt. Biol. Med.	Proceedings of the Society for Experimental Biology and Medicine
Radex Rundschau	Radex Rundschau
Scientia Pharm.	Scientia Pharmaceutica.
Soil Sci.	Soil Science.
Svensk. Kem. Tidskr.	Svensk Kemisk Tidskrift
Tech. Reports Tôhoku Univ.	Technical Reports of Tôhoku University
Trans. Faraday Soc.	Transactions of the Faraday Society
Z. anal. Chem.	Zeitschrift für analytische Chemie
Z. angew. Chem.	Zeitschrift für angewandte Chemie
Z. Elektrochem.	Zeitschrift für Electrochemie (und angewandte physikalische Chemie)
Z. physiol. Chem.	Zeitschrift für physiologische Chemie (Hoppe-Seyler's)
Zhur. analit. Khim.	Zhurnal analiticheskoi Khimii, USSR

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Index

Absorptiometric determination of end-points, 49, 69, 70, 72
Absorption spectrum, of Eriochrome black, 31
  of metalphthalein, 39
  of murexide, 36
  of pyrocatechol violet, 44
Acetate buffers, 17, 58, 77
Acetato-complexes, 7, 77, 90
Acid-base indicators, 46, 57, 78, 80, 81
Acids, polybasic, 2
Alizarin S, 45, 76, 90
Alizarol Cyanon RC, 75
Alkali metals, complexes of, 101
Alkalimetric titrations, 13, 25–8
  curves with EDTA, 25, 26–8, 60, 61
  curves with NITA, 26–8, 61
Alkaline earths, titration curves for, 21
  titration of, 22
  titration of heavy earths with magnesium, 103, 104
Aluminium, back-titration of,
  with iron and salicylic acid, 89–90
  with thorium and Alizarin S, 90
  with zinc and Erio T, 88
  with zinc and dithizone, 90
Amalgam electrodes, 12
Ammine complexes, 3, 13, 17, 79, 83, 99
Amino-acids, as masking-agents, 106
Amino-alcohols, as masking-agents, 106
Amino-malonic acid, 106
Ammoniacal buffers, 4, 11, 17, 58–9
Amperometric titrations, 12
Apparent formation constants, xvii, 6, 11, 13, 16, 21, 24, 25
Apparent indicator constants, 32, 37
Argenticyanide ion, 14, 99
  stability of, 99
Ascorbic acid, 33, 34, 37, 53, 59, 74, 76, 79
Auxiliary complexing agents, 11, 13, 15, 16, 17, 20, 24

Back-titrations, 12, 13, 70, 71, 74, 76, 77, 79, 81, 83, 87, 88, 89, 90, 91, 93, 94, 95, 105
BAL, 52, 59, 62, 64, 69, 73, 86, 93
Barium titration curves for, 19, 66, 72
  effect on colour of indicators, 66, 68, 72
  titration procedures, 66–8, 72
Barium and magnesium, simultaneous determination of, 21, 22
  titration curves, 22
Beryllium, precipitation of, as beryllium ammonium phosphate, 54
  as beryllium hydroxide, 89
Betain structure of EDTA and NITA, 8
Bibliography, 107–25
Bismuth, determination of, 53, 93, 94
Bismuthiiodide ion, as indicator, 45
Bromide, determination of, 14, 98
Bromocresol green, 46, 57
Buffering materials, 16, 17, 19
Buffer mixtures, 4, 58, 59

Cadmium, demasking of cyanide complexes with formaldehyde, 51, 84, 85
  extraction of thiocyanate, 86
  masking with cyanide, 51, 84, 85
  titration in the presence of other metals, 84–7
  titration of, 83, 84

Cadmicyanide ion, stability of, 85
Calcium, direct titration with metalphthalein, 71
  direct titration with murexide, 69
  effect of the colour of indicators, 30, 66, 72
  substitution titration using Erio T, 63
  titration curves, 19, 22, 64, 70
Calcium and magnesium, simultaneous titration of, 21, 23, 64
  titration curves for, 22, 24
Carboxylate ion, as ligand, 7, 102
Catechol (see pyrocatechol)
Caustic soda, standardisation against EDTA, 57
Chelating agent, xv, 3
Chelate complexes, xvii, 3
  higher, 9
  hydrogen, 9
  normal, 9
  stability of, 8
Chelate effect, 2, 3, 4
Chloral hydrate, as de-masking agent, 51, 84
Chloraniline, as buffer, 58, 77
Chloride, determination of, 14, 98
Chromate, indirect determination of, 97
Chromazurol S, 45, 46
Chromotropic acid, 102
Chromotrope 10B, 45, 76
Chromium, titration of, 101
Citrate, as auxiliary complexing agent, 11
Cobalt, titration of, 78, 79, 82
Complex-formation, stepwise, 1, 2, 3
  stoichieometry of, 2
  velocity of, 104, 105
Complexes, higher, 9, 34
  hydroxy-, 9, 18, 19, 23
  ordinary, 1
  penetration, 1
  proton, 9
Complexones, xi, xiii, 6, 55, 104
Complexone I, 56
Complexone III, 55
Complexone IV, 104
Congo-red, as test paper, 74, 75, 78
Copper, determination of, 53, 82
  effect on transition colour of indicators, 80
  extraction of, 54
  titration curves for, 20
  EDTA-complex, as indicator, 49
Coulometric procedures, xi
Cyanide, determination of, 14, 97
  as masking agent, xiv, 33, 41, 51, 59, 62, 64, 69, 73, 74, 76, 77, 85, 91, 92,
  as masking agent for iron, 34, 53, 76
Cyanopalladate ion, 14, 100
Cyanozincate ion, stability of, 85

De-masking, 59, 85, 86
Diamino*cyclo*hexane tetra-acetic acid, 104
  stability of complexes of, 105
Di-(2-aminoethyl) ether-NNN′N′-tetra-acetic acid, 104
  stability of complexes of, 105
Di-(2-aminoethyl) ethyleneglycol-NNN′N′-tetra-acetic acid, 104
  stability of complexes of, 105
Diethyldithiocarbamate, as masking agent, 33, 52, 53
o:o′-Dihydroxy-azodyestuffs, 29
Dimensionless coefficients, xvii, 11, 16, 18, 26, 28
3:3′-Dimethylnaphthidine, 48, 49, 50, 87
Dithiocatechol, 102
Dithizone, 45, 90
1:2-Dimercaptobenzene, 102
2:3-Dimercaptopropanol (see BAL)
Dropping mercury electrode, 1, 12
Dyestuffs, complexes of, 29
  polymerisation of, 30

EDTA (see Ethylenediamine tetra-acetic acid)
Eriochromazurol S, 45, 46, 77, 89
Eriochromeblack dyestuffs, xiii, 29
Eriochrome black T, xiii, 12, 20, 23, 30–5, 50, 62, 63, 66, 67, 74, 76, 79, 81, 83, 85, 87, 91, 92, 100

Eriochrome absorption spectrum, 31
  colour changes with barium and magnesium together, 66
  colour changes with barium and zinc together, 68
  colour changes with calcium, 30, 34, 63
  colour changes with magnesium, 30, 31, 34, 63
  colour changes with strontium and magnesium together, 66
  colour changes with zinc, 30, 33, 34, 80
  pK values, 30
  sensitivity to oxidation, 34
  stock solutions of, 34, 35, 57
Eriochromecyanin R, 46, 75
Ethylenediamine tetra-acetic acid, xv, 6, 7
  as a masking agent, 53, 95
  as a primary standard, 55
  purity of commercial samples of, 55
  salts of, 55
  stability of solutions of, 55
  standard solutions of, 55
  standardisation of volumetric solutions of, 56
Equilibrium constants (see formation constants), xvi

Formation constants, apparent, xvii, 6, 11, 13, 16, 21, 25
  individual (stepwise), xvi, 3
  of cyanide complexes, 85, 86, 99
Fluoride, as masking agent, 33, 37, 52, 59, 77, 80, 82, 83, 87, 88
Formaldehyde, as de-masking agent, 51, 59, 84, 85, 86

Gallium, determination of, 46, 73, 91
Glycine, as buffer component, 58, 77
Gold, determination of, 14, 100
Gross (over-all) stability constants, xvii, 3

Haematoxylin, 45
Halides, titration procedures, 14, 98
Halogens, determination of, 14, 98
Hardness of water, volumetric determination of, xiv, 21, 23, 64
High-frequency conductivity titrations, 12
Higher complexes, of Erio T, 31
Hydroxy-acids, as masking agents, 106
Hydrazine sulphate, as reducing agent, 89
Hydroxy-complexes, 9, 18, 19, 28, 46, 102
  of calcium, 23
  of iron (III), 9, 19, 90
  of magnesium, 23
  of mercury, 9
Hydroxylamine, as reducing agent, 34, 53, 59, 76
8-Hydroxyquinolinates (oxinates), 53, 82

Imidazole, as buffer, 58
Indicators, colour transitions of, 32, 34, 63
Indicator constants, 32, 37
  dependence on pH, 32, 33, 37, 46
Indium, titration of, 46, 73, 91
Indophenol, 48
Infra-red, studies of structures, 9
Interfering anions, removal of, 54
Iodide ion, as indicator, 45, 94
  as masking agent, 52, 80, 88
  determination of, 14, 98
Iodometric determination of metals, 13, 61, 62
Ion-exchange resins, 54
Iron, solvent extraction of, 77
  titration curves for, 20
  determination of, 77, 78

Lead, chlorofluoride, 53
  solvent extraction of, 54
  titration of, 92, 93
Lithium complexes, 101

Magnesium ammonium phosphate, selective precipitation of, 54, 95
Magnesium, determination of, 53, 62
  complexonate, 12, 20, 56, 64, 65, 66, 67, 76, 87, 91, 92
  effect on colour of indicators, 30, 31, 34, 63
  oxalato-complexes of ,62
  standard solutions of, 56
  titration curves for, 19
Magnesium hydroxide, precipitation of, 23, 71
Manganese, determination of, 53, 76
Mannitol, 71
Masking agents, xiv, 33, 51, 52, 53, 59, 102, 106
Mercaptans, as masking agents, 102, 106
  (see BAL)
Mercuric salts, as complexing agents for anions, 102
Mercury, determination of, 87, 88
  hydroxy-complexes, 9
  masking of, 51, 52, 80, 88
Metal indicators, 12, 29–46
  discovery of, xiii
  new types of, 105, 106
Metalphthalein, 38–42, 71, 96, 106
  absorption spectrum of, 38, 39
  colour change with barium, 41, 72
  colour change with calcium, 41, 72
  colour of complexes, 38–40
  stability constants of metal complexes of, 40
  pK values of, 38
  stock solutions of, 42, 57
Methyl red, 46, 81, 87, 89, 91
  stock solutions of, 57
Methyl red—bromocresol green, 46, 57
Milk, determination of calcium and magnesium in, 54
Molybdenum, indirect determination as molybdate, 53
Morin, 46
Murexide, xiii, 35–8, 51, 69, 78, 79, 80, 82, 97, 98, 100
  absorption spectrum, 35, 36
  analysis of preparations, 38
  colour changes with calcium, 34, 35, 36, 66
  colour change with copper, 34, 35, 80
  colour change with nickel, 34, 35, 80
  complex formation with, 37
  apparent indicator constants, 37
  pK values of, 35
  stock solutions of, 38, 57

Naphthol green, 42, 57, 71, 72, 73
"Nervanaid," xi
Nickel, cyanide, 97, 99
  determination of, 53, 79–82
  determination in the presence of cobalt, 82
  effect of the colour of indicators, 34, 80
  titration curves for, 5, 20
  titration with ammonia or polyamines, 4
Nickelocyanide ion, stability of, 86, 98, 99
Niobium, 101
NITA (see nitrilotriacetic acid)
Nitrilotriacetic acid, xv, 6, 7, 13
  as masking agent, 53
  standard solutions of, 27, 56
α-Nitroso-β-naphthol, 82
Nitrophenols, derivatives of, as metal indicators, 106

Overall (gross) stability constants, xvii, 3
Oxidimetric titrations (of manganese and cobalt), 15
Oxalato-complexes, 62
Oxinates, 53, 82

Palladium, determination of, 14, 100
Pectin, indirect determination as calcium pectinate, 53
Penetration complexes, 2

'Penten,' xv, 2
pH-effects, 10, 25–8
pH-indicators, 29, 46, 47
Phenolphthalein, 38, 85
Phosphate, indirect determination of, 14, 53, 95
Photometric titrations, 15, 105
  end-points, 49, 69, 70, 72
Platinum metals, 100, 101, 102
pM-indicators, 29
pM, jump in, during titrations, 4, 12, 18, 19, 22, 79
pM-values, xvi, 4, 12, 16–19
Polyalcohols, as masking agents, 106
Polyamines, as masking agents, xv, 2
  titrations with, 4–6
Polybasic acids, 2
Polyphenols, 2, 102
Polythene vessels, 56
Potentiometric titrations, 12, 13, 78
Pre-titration, 14
Proton-complexes, 8, 9
Purpuric acid, 35
Pyrex glassware, 55
Pyridine thiocyanate complexes, 53
1-(2-Pyridylazo)-2-naphthol, 46
Pyrocatechol, derivatives of, 102
Pyrocatechol violet, 42–5, 75, 77, 83, 93, 94, 106
  absorption spectrum of, 44
  metal complexes of, 43
  bismuth complexes of, 43
  pK values of, 43
  stock solutions of, 45, 57
Pyrophosphate, indirect determination of, 53, 96

Rare-earths, determination of, 73
  separation of, 54
Redox-indicators, 47–8
Redox-potentials of iron complexes, 47
Reductometric titration of manganese, 14
Resins, ion-exchange, 54, 69
Resonating systems, 105

Salicylic acid, as indicator, 42, 45, 74, 77, 89
"Sequestric Acid," xi
Silver, determination of, 14
  indirect titration of, 98
Simultaneous titrations, 21–5, 50, 93
Sodium, complexes of, 101
  indirect titration of, 14, 94
Solvent extraction, 54, 77, 86
Stability constants, (see formation constants)
Step reactions, 1, 2, 3
Strontium, determination of, 66, 67, 72, 73
  effect of colour of indicators, 66
Strontium and magnesium, simultaneous titration of, 22
  titration curves for mixture of, 22
Substitution of zinc by barium, 24
Substitution titrations, 12, 21, 66, 76, 87, 91, 92, 103
Sucrose, 70, 71
Sulphate, determination of, 14, 96, 97
Sulphosalicylic acid, 45
Sulphides, as masking agents, 33, 52, 59, 62, 64, 73
  determination of, 96
Sulphur, determination of, 14, 67, 96, 97

Tartrate, as auxiliary complexing agent, 11, 76, 91, 92
NNN'N'-Tetra(β-aminoethyl) ethylenediamine, ('penten'), 2–6
Tetracyanonickelate ion, 14, 97, 98, 99
Thallium, determination of, 91, 92
Thio-complexes, 101, 102
Thiocyanate, determination of, 14, 98
  as indicator, 45, 77
Thiourea, as indicator, 45, 94
  as masking agent, 86
Thorium, determination of, 75, 76
  stability of EDTA complexes of, 9

Tiron, 42, 77
  as masking agent, 33, 51, 76, 83
  indicator constants of, 42,
  iron complexes of, 42
  stock solutions of, 42, 57
Titanium, complex with EDTA, 102
Titration, alkalimetric, for metals, 25–8, 60–2
  curves, 4, 5, 15–28
  direct, 11, 15
  of mixtures, 50–4
  of precipitates, 14, 81, 95, 96, 98
'Tren', xv, 2, 3
Tri-(2-aminoethyl) amine, ('tren'), xv, 2, 3
Triethanolamine, as buffer component, 58, 74
  as chelating agent, 37, 58, 76, 92
  as masking agent, 33, 37, 51, 69, 70, 74, 76, 79, 92
Tris-(β-mercaptoethyl) phosphine, 102
Tungsten, indirect determination of, 53

Uramil diacetic acid, xiii, 101

Vanadium, determination of, 101
Variamine blue, 47, 48, 78
"Versenes," xi, 55

Water, determination of hardness, xiv, 21, 23, 64

Zinc, complexonate, 20, 56, 67
  demasking of cyanide complex of, 84, 85, 86
  determination of, 48, 83–7
  effect on colour of indicators, 30, 80
  solvent extraction of, 54, 86
  masking with cyanide, 85, 86
  standard solution of, 56
  titration of, in the presence of other metals, 84–6
  titration curves for, 20
Zincon, 46, 84
Zirconium, determination of, 74

P

4487